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Supramolecular Substitution Reactions between Hydrazide-Based Molecular Duplex Strands: Complexation Induced Nonsymmetry and Dynamic Behavior

Yong Yang, Jun-Feng Xiang, Min Xue, Hai-Yu Hu, and Chuan-Feng Chen*

Beijing National Laboratory for Molecular Sciences, Center for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

cchen@iccas.ac.cn

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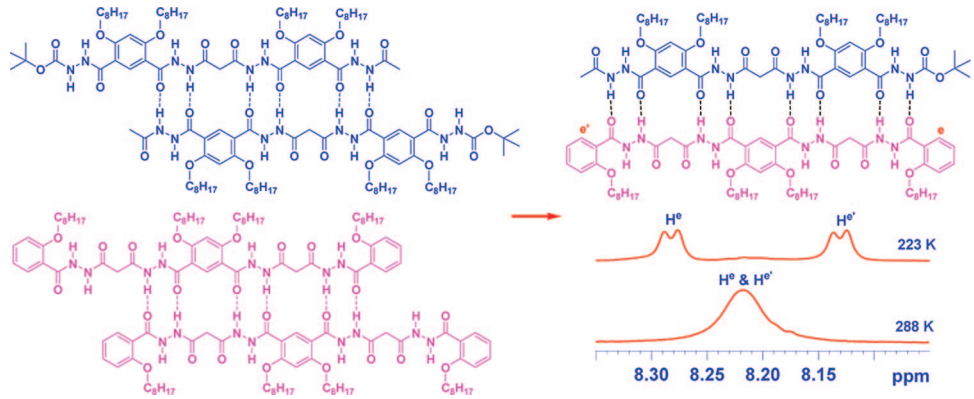

Supramolecular substitution reactions between hydrazide-based oligomers **1a**−**c** and **2a**−**c** were systematically investigated. Each oligomer existed as hydrogen-bonding mediated molecular duplex strands or a polymeric zipper structure in apolar solvents. But when another oligomer with complementary hydrogen bonding sites was added, a heterodimer structure formed due to supramolecular substitution reaction driven by the formation of more hydrogen bonds, which was evidenced by NMR experiments, sometimes gel−sol transition. When a nonsymmetric oligomer and a symmetric oligomer were involved, complexation-induced nonsymmetry was observed. When two nonsymmetric oligomers were involved, two hydrogen-bonded isomers were observed in solution. Variable-temperature ^{1}H NMR experiments further revealed unique dynamic behavior for the individual oligomer and the complexes. When diacetyl-terminated oligomer **1c** was involved, slides perpendicular to hydrogen bonds between two constituent molecules were observed, which led to complicated ^{1}H NMR spectra at lower temperature; otherwise, high selectivity was obtained. Combined with the results we reported previously, a detailed picture of the structure−property relationship for our hydrazide-based oligomers was depicted, which would provide guidelines for the design of hydrazide-based fine-tuning functional materials.

Introduction

In nature, cooperative action of numerous noncovalent forces leads to highly specific molecular recognition events and subsequently precise and elegant functions.[1] Cooperative action of many noncovalent attractions also renders well-defined three-dimensional shapes of biomolecules and various nanoscale structures in biological systems. However, it is a daunting challenge for chemists to synthesize high-order structures with comparable dimensions and functions even with the best present-day synthetic methods. This situation will be greatly changed if a diverse set of specific recognition events or self-associating modules become available. Among the many biostructures, discovery of the double-helical structure of DNA[2] via hydrophobic effects, hydrogen bonds, and $\pi-\pi$ stacking interactions and elucidation of its function of genetic information carrier

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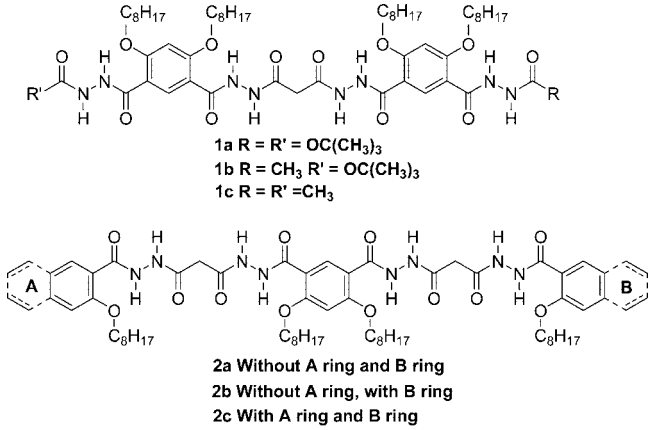

FIGURE 1. Chemical structures of hydrazide-based oligomers **1a**−**c** and **2a**−**c** used in this study.

have formed the basis of modern molecular biology.[3] Recent studies revealed that protein secondary structure β-sheet played an important role in many diseases, such as Alzherimer's disease, the prion disease, and other neurodegenerative disorders.[4] Other double- and multiple-stranded complexes self-assembled from linear oligomers with encoded recognition sites are ubiquitous in nature, which are the foundation of other higher structures and functions of biomolecules. Inspired by the elegant functions of these structures in nature and for scientific and aesthetic reasons, there is currently intensive focus of chemical research on the construction of stable molecular duplex strands from unnatural backbones for structure mimicking and potential applications.[5]

Hydrogen bonding, as adopted by natural DNA, characteristic of strength and directionality,[6] has been described as the "masterkey interaction in supramolecular chemistry"[7] and is an ideal noncovalent interaction for this mission. Hydrogen-bonding modules assembled with high stability, fidelity, and selectivity are favored in this field. Heterocycle-based building blocks (usually urea derivatives)[8–19] and linear materials composed of arrays of hydrogen-bonding sites[20–28] have gained great success.

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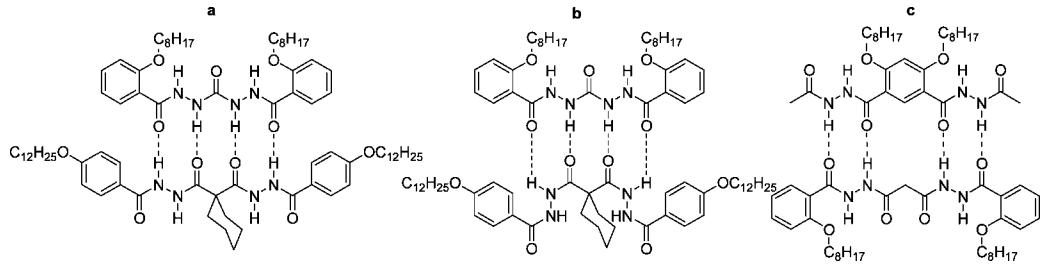
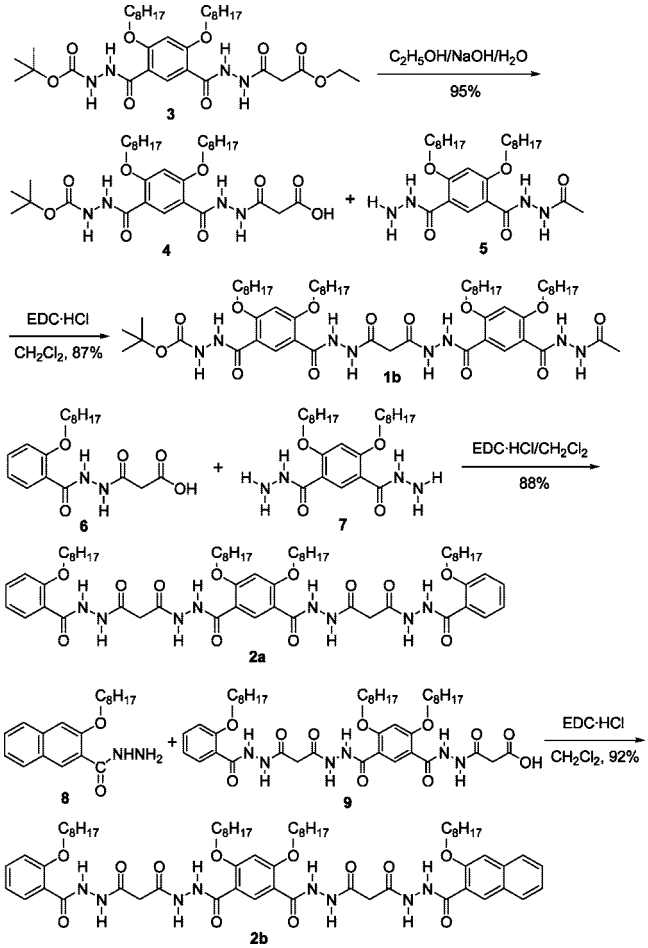
CHART 1. Representation of Li's Hydrazide-Based Quadruply Hydrogen-Bonded Heterodimers (a, b)[22] and Ours (c)[34]



SCHEME 1. Synthetic Routes for 1b, 2a, and 2b



In particular, Meijer's ureidopyrimidone (UPy) building block,[11,29] with its characteristic simplicity in synthesis and exceedingly high dimerization constant ($K_{dim} \sim 10^7$ M^{-1} in $CDCl_3$), has found widespread applications in the construction of various nanostructures,[30] material science,[31] separation,[32] catalysis,[33] etc. Gong's oligoamide system[20] and Zimmerman's ureidonaphthyridine system[25] are successful examples of other building blocks. Considering their widespread applications, the number of this kind of hydrogen-bonding building blocks available for use is limited. Therefore, there is a strong need to develop such hydrogen-bonding motifs, especially motifs with programmable strength and specificity as demonstrated by natural biomolecules. Investigations along this route will provide mimics of biomolecules and shed some light on the understanding of the complicated structures and functions as demonstrated by them. Eventually, new materials with functional properties can also be expected from these unnatural counterparts.

Recently, Li et al. reported a new type of hydrazide-based quadruply hydrogen-bonded heterodimer system (Chart 1),[22] in which S(6)-type hydrogen bonding and a bulky cyclohexyl group were introduced to preorganize hydrogen-bonding sites and to block unwanted hydrogen-bonding sites, even though two hydrogen-bonded isomers were observed in solution. Similarly, by introduction of S(6)-type hydrogen bonding to preorganize hydrogen bonding sites and to block unwanted hydrogen-bonding sites, we[34] also reported a new kind of hydrazide-based quadruply hydrogen-bonded hererodimer with geometrically complementary *m*-phenylene and malonyl groups as spacers (Chart 1). The only heterodimer structure was exclusively observed in solution. Based on the study of this model system, we[34] further constructed a new family of hydrogen-bonded molecular duplex strands from self-assembly of hydrazide-based oligomers by applying "covalent casting"[21] to a hydrazide-based one-dimensional hydrogen-bonding motif.[35,36] Different dynamic behavior and association constants were observed for acetyl-terminated series and Boc-terminated series. From di-Boc-terminated series, variable-temperature ^{1}H NMR experiments revealed a shuttle-like dynamic process of the two constituent molecules of the duplex strands.[37] Molecular mechanical calculations revealed double-helical structures for

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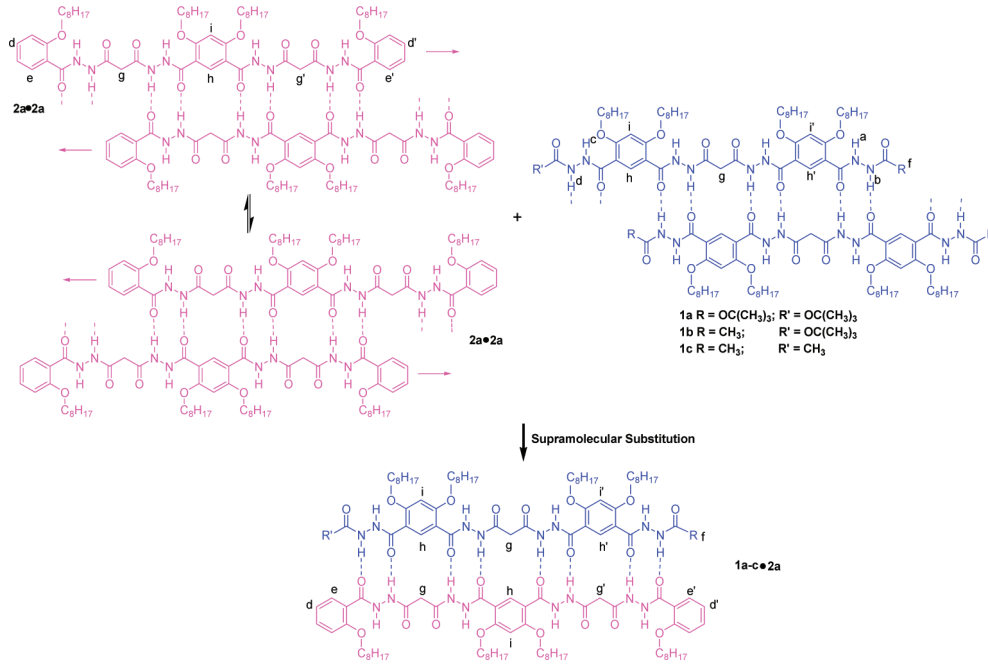

FIGURE 2. Representation of shuttle-like dynamic process of **2a**·**2a** and supramolecular substitution reactions between **1a**−**c** and **2a**.

the duplex strands.[34,37] Gelation was observed with diacetyl-terminated **1c** and dinaphthyl-terminated **2c**. A multipoint recognition-directed supramolecular substitution reaction led to mutual responsive LMOGs, and variable-temperature ^{1}H NMR experiments revealed unique dynamic behavior for the complex.[38] In this paper, we will systematically investigate supramolecular substitution reactions between **1a**−**c** and **2a**−**c** (Figure 1). Dynamic behavior for each duplex strands is also explored. Combined with the results we reported previously, we try to depict a detailed picture of the structure−property relationship for our hydrazide-based oligomers, which, we believe, will provide guidelines for the design of hydrazide-based fine-tuning functional materials.

Results and Discussion

Synthesis. Compounds **1a**,[37] **1c**,[38] and **2c**[38] were synthesized previously. Compound **1b** was synthesized via coupling reaction of compound **4** and compound **5**,[34] while compound **4** was obtained via hydrolysis of compound **3**.[34] Compounds **2a** and **2b** were synthesized via coupling reactions of **6**[34] and **7**[34] and **8**[38] and **9**,[34] respectively (Scheme 1). EDC·HCl was found to be an efficient coupling reagent for the reaction between carboxylic acid and hydrazide derivatives. In all cases, high yields were obtained.

Supramolecular Substitution Reactions between 2a and 1a−c. Though ubiquitous and very important for many biological processes in nature, multipoint recognition presents a great challenge for chemists. As we reported previously, a multipoint recognition-directed supramolecular substitution reaction between **1c** and **2c** led to gel−sol transition.[38] In this paper, we tried to investigate supramolecular substitution reactions such as $\mathbf{X}\cdot\mathbf{X} + \mathbf{Y}\cdot\mathbf{Y} \rightarrow 2\mathbf{X}\cdot\mathbf{Y}$ or $\mathbf{X}_n + \mathbf{Y}_n \rightarrow n\mathbf{X}\cdot\mathbf{Y}$ or $2\mathbf{X}_n + n\mathbf{Y}\cdot\mathbf{Y} \rightarrow 2n\mathbf{X}\cdot\mathbf{Y}$ systematically and exhaustively between **1a**−**c** and **2a**−**c**, which possessed complementary hydrogen bonding sites. First, as in the case of **1c** and **2c**, addition of an equimolar **2a** into the viscous solution from **1c** in $CHCl_3$ resulted in a clear solution. This phenomenon might suggest that the polymeric zipper structure derived from **1c** disrupted upon interaction with **2a** to form a discrete heterodimer structure (Figure 2). ^{1}H NMR mixing experiments and 2D NOESY experiment further confirmed the hypothesis. The ^{1}H NMR spectrum of **1c** alone in $CDCl_3$ at 10 mM cannot be recorded because the solutin is very viscous. But a clear solution of **1c** and **2a** in $CDCl_3$ (each 10 mM) gave a well-resolved spectrum (Figure 3f). A cross contact between terminal methyl protons **1c**-H^f and **2a**-H^e (H$^{e'}$) was undoubtedly observed in the 2D NOESY spectrum (Figure 4b). Variable-temperature ^{1}H NMR experiments revealed unique dynamic behavior. A similar shuttle-like dynamic process for di-Boc-terminated series[37] was observed for **2a**. At 298 K, a dimerization self-assembly mode for **2a** was undoubtedly established by 2D NOESY experiments (Figure 4a). Cross

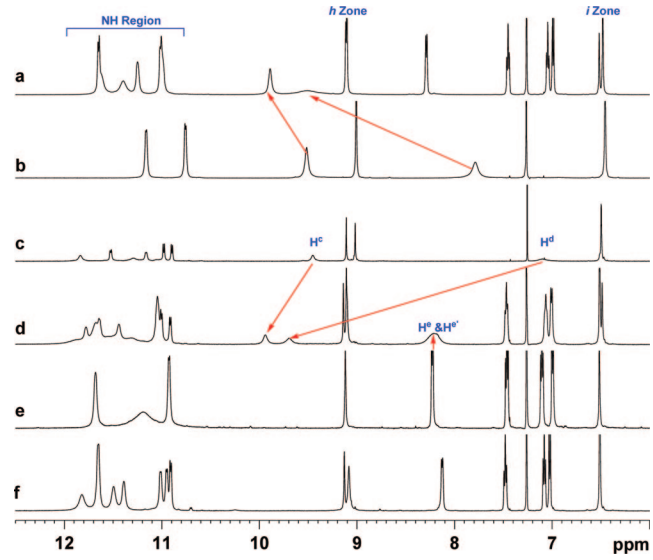

FIGURE 3. Stacked partial ^{1}H NMR spectra of (a) **1a** and **2a**, (b) **1a**, (c) **1b**, (d) **1b** and **2a**, (e) **2a**, and (f) **1c**and **2a** at 298 K, 600 MHz, each 10 mM in $CDCl_3$.

(38) Yang, Y.; Chen, T.; Xiang, J.-F.; Yan, H,-J.; Chen, C.-F.; Wan, L.-J. *Chem. Eur. J.* **2008**, *14*, 5742–5746.

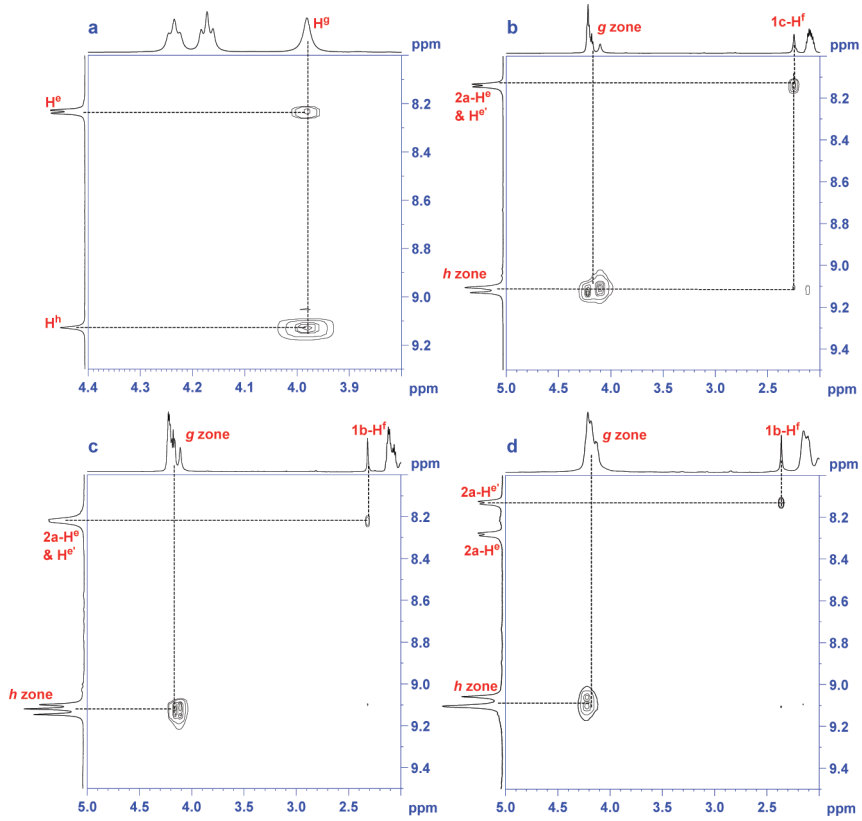

FIGURE 4. 2D NOESY spectra of (a) **2a**, 298 K, (b) **1c** and **2a**, 298 K, (c) **1b** and **2a**, 298 K, and (d) **1b** and **2a**, 223 K, each 10 mM in $CDCl_3$, 600 MHz.

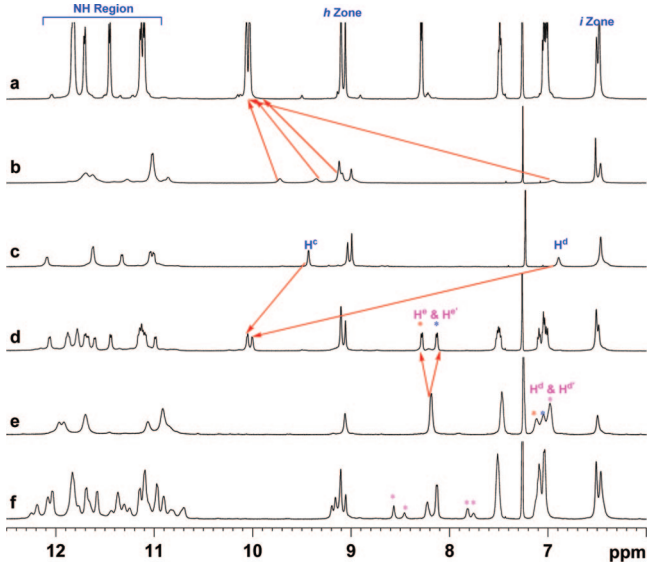

FIGURE 5. Stacked partial ^{1}H NMR spectra of (a) **1a** and **2a**, (b) **1a**, (c) **1b**, (d) **1b** and **2a**, (e) **2a**, and (f) **1c** and **2a** at 223 K, 600 MHz, each 10 mM in $CDCl_3$.

contacts between H^g and H^h andH^g ($H^{g'}$) and H^e ($H^{e'}$) were observed. At 223 K, a signal corresponding to methylene protons (*g* zone) of malonyl groups split into two peaks: one shifted downfield and one shifted upfield. Partial signals for NHs also displayed upfield shift. Terminal aromatic protons displayed broad signals. Two sets of signals were observed for H^d and $H^{d'}$ (Figure 5e). All of these findings are consistent with a shuttle-like dynamic process as depicted in Figure 2. When a mixture of **1c** and **2a** in $CDCl_3$ (each 10 mM) was analyzed at lower temperature (Figure 5f), multiple sets of signals were observed in the NH region between 10.9 and 12.6 ppm. New minor signals also appeared in the area between 7.5 and 8.5 ppm, which might correspond to NHs not involved in hydrogen bonding. These findings might suggest intermolecular slide perpendicular to hydrogen bonds as observed for acetyl terminated series[34] and **1c**·**2c**.[38] 2D NOESY experiments (Figure 4b) also provided another evidence for the conclusion: a minor cross contact between **1c**-H^f and the *h* zone was clearly observed.

Supramolecular substitution reactions between **1a** and **2a** and **1b** and **2a** were also analyzed by ^{1}H NMR and 2D NOESY experiments. Substantial downfield shifts (>2 ppm) were observed for the NHs (H^d) adjacent to Boc groups in the ^{1}H NMR spectra of 1:1 mixtures in $CDCl_3$ (each 10 mM) at 298 K (Figure 3a and 3d), which might indicate strong intermolecular association. Intensive contacts were observed between *g* zone and *h* zone in the 2D NOESY spectra.[39] Especially for a mixture of **1b** and **2a**, a cross contact between terminal methyl groups **1b**-H^f and **2a**-H^e ($H^{e'}$) was observed (Figure 5c), which provided diagnostic evidence for the heterodimer structure. With lowering of temperature in the ^{1}H NMR spectrum (Figure 5a) of 1:1 mixture (each 10 mM) of **1a** and **2a**, only NHs adjacent to Boc groups displayed signal sharpening and minor position shifts. In the case of nonsymmetric oligomer **1b** and symmetric oligomer **2a** (1:1 mixed, each 10 mM in $CDCl_3$), complexation-induced nonsymmetry was observed. Signals for terminal aromatic protons of **2a** displayed broad peaks at 298 K and two sets of peaks at 223 K, especially those for H^e and $H^{e'}$ (Figure 5d). 2D NOESY experiment at 223 K revealed that the

(39) See the Supporting Information for more details.

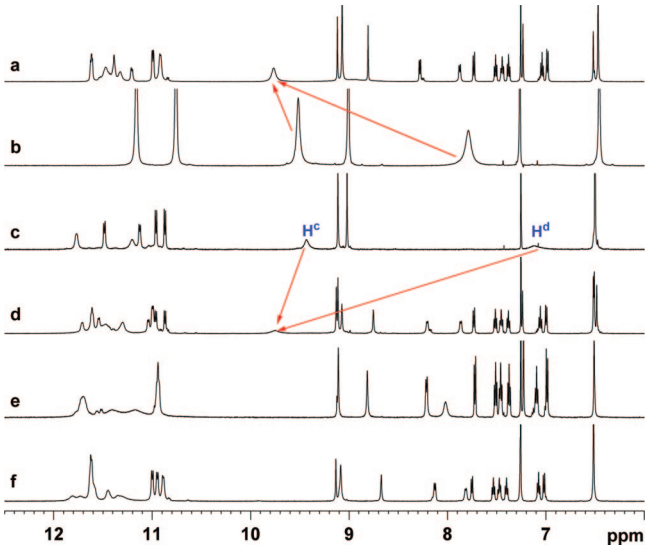

FIGURE 6. Stacked partial ^{1}H NMR spectra of (a) **1a** and **2b**, (b) **1a**, (c) **1b**, (d) **1b** and **2b**, (e) **2b**, and (f) **1c** and **2b** at 298 K, 600 MHz, each 10 mM in $CDCl_3$.

terminal methyl group **1b**-H^f only contacted with **2a**-$H^{e'}$ (Figure 4d). These findings can be rationalized by considering the eight hydrogen-bonded complex **1b**·**2a** as a covalently bonded molecule: the nonsymmetric nature of **1b** induced nonsymmetry of **2a** upon complexation, just as one component of a molecule induced nonsymmetry of another component of the same molecule.

Supramolecular Substitution Reactions between 2b and 1a−c. Supramolecular substitution reactions between **1a−c** and **2b** and dynamic behavior of the complexes were also analyzed by NMR experiments. As found in the cases of **1c** and **2a** (vide supra) and **1c** and **2c**,[38] addition of one equimolar **2b** into the viscous solution of **1c** in $CDCl_3$ also resulted in a clear solution, and ^{1}H NMR experiments revealed a well-resolved spectrum (Figure 6f). Cross contacts between **1c**-H^f and **2b**-H^d, **2b**-H^e were undoubtedly observed in the 2D NOESY spectrum, and contact between **1c**-H^f and *h* zone was also observed (Figure 7b). These findings might indicate slide between the two constituent molecules of the complex, which was further confirmed by variable-temperature ^{1}H NMR experiments (vide infra). 2D NOESY experiments on **2b** (10 mM in $CDCl_3$) revealed contacts between H^d, H^e, H^h, and *g* zone (Figure 7a). In the ^{1}H NMR spectrum of **2b** at 223 K (Figure 8e), multiple sets of signals were observed, especially two signals for H^h and three signals for H^e ($H^{e'}$). On thes basis of these findings, a complicated equilibrium for **2b** in $CDCl_3$ as depicted in Figure 9 was proposed. Form **X** and form **X′**, form **Y** and form **Y′** are degenerated states, and there exist shuttle-like dynamic processes as observed for di-Boc-terminated series[37] and **2a** (vide supra), while form **X**, form **X′**, and form **Y**, form**Y′** can be viewed as hydrogen-bonding isomers. Variable-temperature ^{1}H NMR experiments on a 1:1 mixture of **1c** and **2b** (each 10 mM in $CDCl_3$) revealed dynamic behavior for the complex similar to those for complexes **1c**·**2a** (vide supra), **1c**·**2c**,[38] and acetyl-terminated series:[34] multiple sets of signals were observed at 223 K (Figure 8f). Complexation-induced nonsymmetry was also observed with nonsymmetric **2b** and symmetric **1a**. At 298 K, there were two peaks with an intensity ratio of 1:2, each presenting in the *h* zone and *i* zone of ^{1}H NMR spectrum of 1:1 mixture of **2b** and **1a**, and NHs adjacent to the Boc groups displayed broad signals at about 9.75 ppm (Figure 6a), while at 223 K, three peaks with an intensity ratio of 1:1:1 each presenting in the *h* zone and *i* zone and NHs adjacent to the Boc groups displayed four sharp signals (Figure 8a). These temperature-dependent changes may also be attributed to nonsymmetry of **1a** upon complexation with nonsymmetric **2b**. When two nonsymmetric oligomers **1b** and **2b** were involved, the 2D NOESY spectrum (298 K) revealed contacts between **1b**-H^f and **2b**-H^e, **1b**-H^f and **2b**-H^d (Figure 7c). There should exist two isomers **1b**·**2b** and (**1b**·**2b**)′ for the heterodimer, as depicted in Figure 9. Variable-temperature ^{1}H NMR experiments on a 1:1 mixture of **1b** and **2b** further confirmed our hypothesis. At 223 K, two sets of signals were observed, especially those for NHs adjacent to Boc group, **2b**-H^e ($H^{e'}$) and **2b**-H^d ($H^{d'}$), **1b**-H^f ($H^{f'}$), *h* zone, and *i* zone (Figure 8d). In the 2D NOESY spectrum of 1:1 mixed **1b** and **2b** in $CDCl_3$ (each 10 mM) at 223 K, contacts between **1b**-$H^{f'}$ and **2b**-H^d, **1b**-H^f and **2b**-H^e were observed (Figure 7d), which provided another diagnostic evidence for the existence of two hydrogen bonded isomers. These findings suggest that exchange process between the two hydrogen bonding isomers **1b**·**2b** and (**1b**·**2b**)′ are prohibited or slow on the NMR time scale at this temperature. The ratio for the two isomers is **1b**·**2b**:(**1b**·**2b**)′ = 2:3 (results based on integration of signals for H^e and $H^{e'}$, H^d and $H^{d'}$ at 223 K). A slight selectivity was obtained.

Supramolecular Substitution Reactions Between 2c and 1a−c. When we systematically investigated supramolecular substitution reactions between **1a−c** and **2c**, different results were obtained. As reported previously, 10 mM (ca. 0.8%, w/w) **2c** in $CHCl_3$ formed a gel, and addition of equimolar another gelator **1c** led to gel−sol transition.[38] Variable-temperature ^{1}H NMR experiments revealed slides perpendicular to hydrogen bonds between the two constituent molecules of the complex (Figure 10c,d). Addition of equimolar **1a** into the gel from **2c** in $CDCl_3$ also led to gel−sol transition, and the complex **1a**·**2c** displayed a well-resolved spectrum (Figure 10a). The NHs of **1a** adjacent to Boc displayed large downfield shifts and lowering of temperature only led to signal sharpening and minor shifts (Figure 10a,b).[41] To our surprise, 1:1 mixed **1b** and **2c** in $CDCl_3$ could not lead to a gel−sol transition[39] as in the cases of **1a**·**2c** and **1c**·**2c**. This exceptional case might need further investigation.

Conclusions

In conclusion, we systematically and exhaustively investigated supramolecular substitution reactions between hydrazide-based oligomers with complementary hydrogen-bonding sites. In particular, when a symmetric oligomer and a nonsymmetric oligomer were involved, complexation-induced nonsymmetry was observed, just as one component of a molecular induced nonsymmetry of another component of the same molecule: cooperative action of multiply hydrogen bonds can be as strong as covalent bonds; when two nonsymmetric oligomers were involved, two hydrogen-bonded isomers were observed. Dynamic behavior for the molecular duplex strands was also investigated by variable-temperature ^{1}H NMR experiments.

(40) (a) Wilcox, C. S. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Durr, H. Eds.; VCH: New York, 1991; pp 123−143. (b) Conners, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley-Interscience: New York, 1987.

(41) In the variable-temperature ^{1}H NMR spectra for C2·H3, signals in the h zone and i zone split into three peaks. We do not understand the reasons for this phenomenon at present. Perhaps this comes from the double helical conformation of the complex. See the Supporting Information for more details.

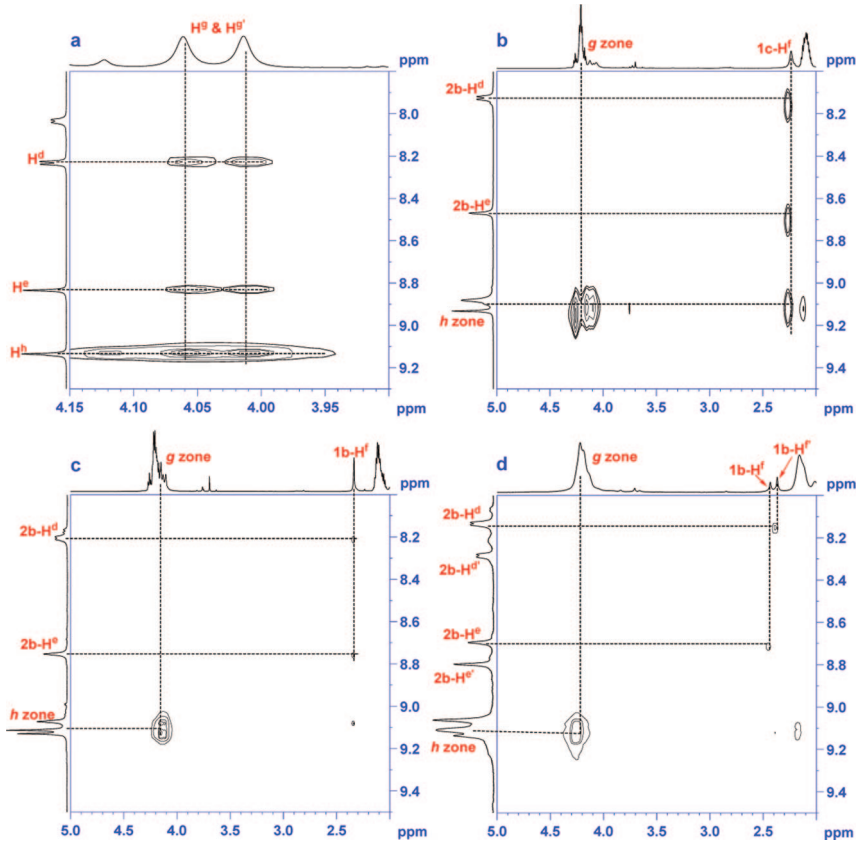

FIGURE 7. 2D NOESY spectra of (a) **2b**, 298 K, (b) **1c** and **2b**, 298 K, (c) **1b** and **2b**, 298 K, and (d) **1b** and **2b**, 223 K, each 10 mM in $CDCl_3$, 600 MHz.

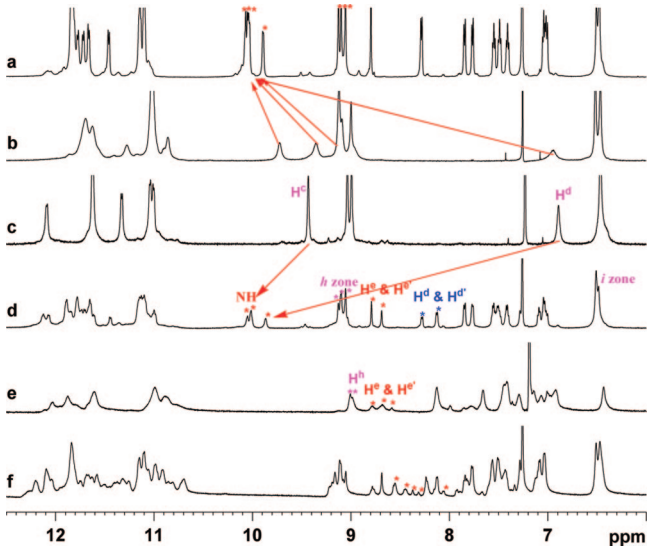

FIGURE 8. Stacked partial ^{1}H NMR spectra of (a) **1a** and **2b**, (b) **1a**, (c) **1b**, (d) **1b** and **2b**, (e) **2b**, and (f) **1c** and **2b** at 223 K, 600 MHz, each 10 mM in $CDCl_3$.

Combined with the results we reported previously, by systematic modification on the structures, a detailed picture of structure−property relationship for our hydrazide-based molecular duplex strands can be depicted: (1) Boc groups affect the dynamic behavior of the molecular duplex strands substantially: when a Boc group is involved, high selectivity is obtained; otherwise, slide perpendicular to the hydrogen bonds leads to a complicated ^{1}H NMR spectrum at low temperature, which might come from a dimer−polymer equilibrium; (2) spectator secondary electrostatic repulsive interaction inherent with Boc group can affect the association stability of the molecular duplex strands; and (3) gelation is observed with diacetyl-terminated oligomer **1c** and dinaphthyl-terminated oligomer **2c**, and supramolecular substitution reaction leads to mutual responsive LMOGs. We believe that the structure−property relationship revealed here will provide guidelines for the design of hydrazide-based fine-tuning functional materials, the development of environment-responsive supramolecular polymers, and the construction of complex supramolecular structures, which are underway in our laboratory.

Experimental Section

Synthesis of Compound 4. To a suspension of compound **3** (1.33 g, 2 mmol) in C_2H_5OH (15 mL) was added a solution of NaOH (0.24 g, 6 mmol) in 15 mL of water. The mixture was then stirred at room temperature, and the reaction was monitored by TLC. The reaction was complete in 5 h. The organic solvent was evaporated under reduced pressure, and the residue was acidified with concentrated HCl. Upon acidification, a white solid precipitated from the solution and the crude product was collected by filtration. The pure product as a white solid was obtained by recrystallization from hot acetonitrile (1.21 g, 95%). Mp: 163−164 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, TMS): δ 12.49 (s, 1H, COO*H*), 10.96 (d, J = 3.7 Hz, 1H, *H*-N), 10.20 (d, J = 3.2 Hz, 1H, *H*-N), 9.40 (s, 1H, *H*-N), 9.02 (s, 1H, *H*-Ar), 8.33 (s, 1H; *H*-N), 6.81 (s, 1H, *H*-Ar), 4.29−4.22 (m, 4H, OCH_2), 3.31 (s, 2H, COCH_2CO), 1.88−1.77 (m, 4H, CH_2), 1.43−1.26 (m, 29H, CH_2 and OC(CH_3)$_3$), 0.86 (t, J = 6.9 Hz, 5.1 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K, TMS): δ 168.8, 164.2, 162.3, 160.6, 160.3, 160.0, 155.1, 134.1, 114.0, 112.4, 97.8, 79.1, 69.6, 69.3, 31.23, 31.19, 28.8, 28.63, 28.61, 28.3, 28.0, 25.5, 22.09, 22.06, 13.89, 13.88. IR (KBr, cm^{-1}): 3369,

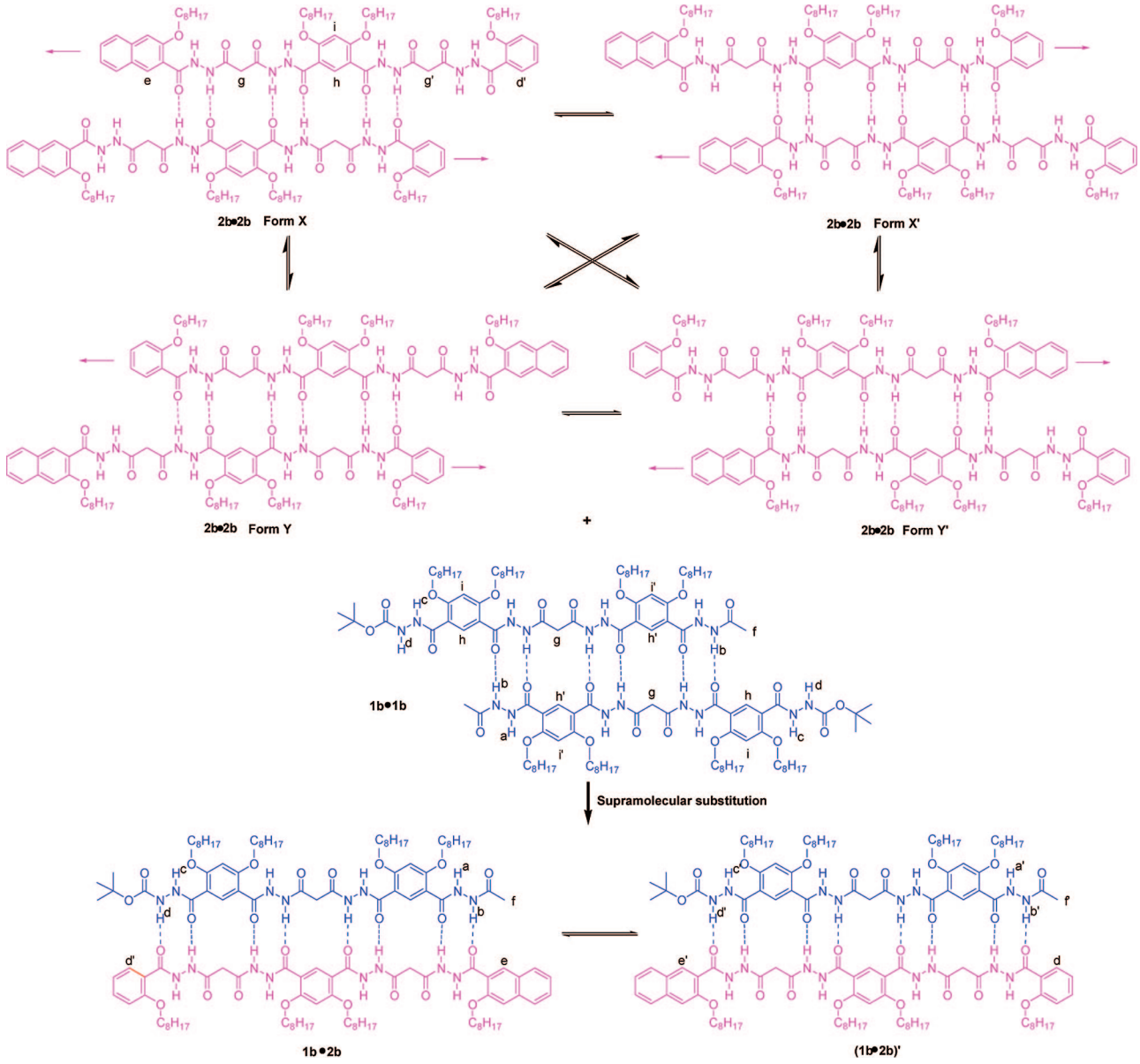

FIGURE 9. Representation of equilibrium for **2b** in $CDCl_3$ and supramolecular substitution reaction between nonsymmetric monomers **1b** and **2b**.

3317, 3219, 2926, 2859, 1740, 1713, 1616, 1467 cm^{-1}. MS (MALDI-TOF): *m/z* 659.1 $[M + Na]^+$, 675.0 $[M + K]^+$. MS (ESI): *m/z* 635.06 $[M - H]^-$. Anal. Calcd for $C_{32}H_{52}N_4O_9$: C, 60.36; H, 8.23; N, 8.80. Found: C, 60.21; H, 8.27; N, 9.14.

Synthesis of 1b. To a solution of compound **4** (255 mg, 0.4 mmol) and compound **5** (197 mg, 0.4 mmol) in CH_2Cl_2 with cooling in an ice−water bath was added EDC·HCl (116 mg, 0.6 mmol). The mixture was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from hot acetonitrile to give the product as a white solid (0.38 g, 87%). Mp: 132−133 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ 11.78 (d, J = 8.0 Hz, 1H, N-*H*), 11.49 (d, J = 8.3 Hz, 1H, N-*H*), 11.22 (d, J = 8.2 Hz, 1H, N*H*), 11.14 (d, J = 8.1 Hz, 1H, N*H*), 10.97 (d, J = 8.2 Hz, 1H, N-*H*), 10.88 (d, J = 8.1 Hz, 1H, N-*H*), 9.43 (s, 1H, N-*H*), 9.12 (s, 1H, Ar-*H*), 9.03 (s, 1H, Ar-*H*), 7.22−7.05 (br, 1H, N-*H*), 6.51 (s, 2H, Ar-*H*), 4.25−4.10 (m, 10H, OCH_2 and $COCH_2CO$), 2.38 (s, 3H, $COCH_3$), 2.15−1.93 (m, 8H, CH_2), 1.55−1.20 (m, 49H, CH_2 and $OC(CH_3)_3$), 0.90−0.83 (m, 12H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, TMS): δ 165.2, 162.9, 160.9, 160.8, 160.5, 157.2, 157.0, 155.1, 136.8, 112.9, 112.3, 111.9, 96.3, 81.3, 70.3, 38.9, 31.7, 29.3, 29.2, 29.1, 29.0, 28.8, 28.6, 28.2, 26.1, 26.0, 25.9, 25.8, 22.6, 20.6, 14.1. IR (KBr, cm^{-1}): 3344, 3227, 2928, 2859, 1631, 1458 cm^{-1}. MS (ESI): *m/z* 1110.09 $[M]^-$. Anal. Calcd for $C_{58}H_{94}N_8O_{13}$: C, 62.68; H, 8.52; N, 10.08. Found: C, 62.61; H, 8.48; N, 10.22.

Synthesis of 2a. To a solution of compound **6** (0.56 g, 1.6 mmol) and compound **7** (0.36 g, 0.8 mmol) in CH_2Cl_2 with cooling in an ice−water bath was added EDC·HCl (0.38 g, 2.0 mmol). The mixture was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from hot acetonitrile to give the product as a white solid (0.78 g, 88%). Mp: 95−96 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ 11.64 (s, 2H, *H*-N), 11.38 (s, 2H, *H*-N), 11.13 (s, 2H, *H*-N),10.92 (s, 2H, *H*-N), 9.13 (s, 1H, *H*-Ar), 8.83 (s, 1H, *H*-Ar), 8.23 (d, J = 7.7 Hz, 1H, *H*-Ar), 8.03 (d, J = 7.8 Hz, 1H, *H*-Ar), 7.73 (d, J = 8.1 Hz, 1H, *H*-Ar), 7.54−7.23 (m, 3H, *H*-Ar), 7.24 (s, 1H, *H*-Ar), 7.10 (t, J = 7.6 Hz, 1H, *H*-Ar), 7.00 (d, J = 8.5 Hz, 1H, *H*-Ar), 6.53 (s, 1H, *H*-Ar), 4.29−4.14 (m, 8H, OCH_2), 4.06 (s, 2H, $COCH_2CO$), 4.01 (s, 2H, $COCH_2CO$), 2.12−2.00 (m, 8H, CH_2), 1.54−1.26 (m, 40H, CH_2), 0.90−0.75 (m, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, TMS): δ 161.3, 161.1, 160.8, 160.7, 159.6, 159.0, 157.6, 157.5, 157.1, 153.9, 137.0, 136.0, 133.9, 133.4, 132.0,

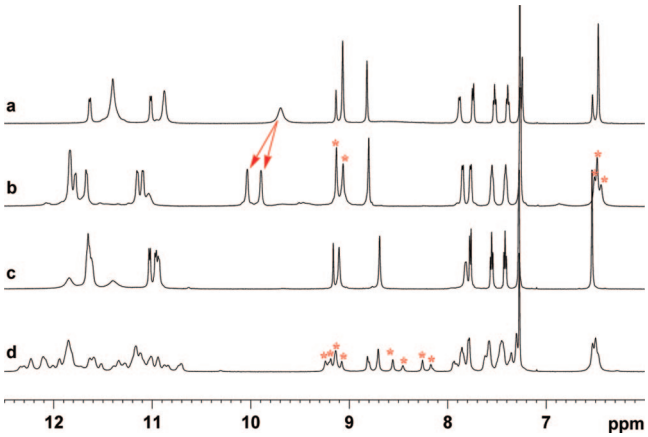

FIGURE 10. Stacked partial ^{1}H NMR spectra of (a) **1a** and **2c**, 298 K, (b) **1a** and **2c**, 223 K, (c) **1c** and **2c**, 298 K, and (d) **1c** and **2c**, 223 K, 600 MHz, each 10 mM in $CDCl_3$.

129.5, 128.5, 128.2, 126.1, 124.6, 121.2, 119.7, 118.9, 112.2, 111.8, 111.7, 107.4, 96.3, 70.4, 69.6, 52.4, 39.0, 31.8, 29.29, 29.25, 29.15, 28.84, 28.77, 26.1, 26.0, 22.6, 14.1. IR (KBr): ν = 3347, 3223, 2926, 2858, 1627, 1461 cm^{-1}. MS (MALDI-TOF): *m/z* 1187.7 [M + Na]$^+$, 1203.6 [M + K]$^+$. Anal. Calcd for $C_{64}H_{92}N_8O_{12}$: C, 65.96; H, 7.96; N, 9.61. Found: C, 65.37; H, 8.08; N, 9.95.

Synthesis of 2b. To a solution of compound **8** (126 mg, 0.4 mmol) and compound **9** (347 mg, 0.4 mmol) in CH_2Cl_2 with cooling in an ice−water bath was added EDC·HCl (96 mg, 0.5 mmol). The mixture was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from hot acetonitrile to give the product as a white solid (0.42 g, 92%). Mp: 175−176 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ 11.61−11.52 (br, 2H, *H*-N), 11.16−11.03 (br, 4H, *H*-N), 10.87 (s, 2H, *H*-N), 9.12 (s, 1H, *H*-Ar), 8.23 (d, J = 7.2 Hz, 2H, *H*-Ar), 7.46 (t, J = 8.0 Hz, 2H, *H*-Ar), 7.10 (t, J = 7.5 Hz, 2H, *H*-Ar), 6.99 (d, J = 8.4 Hz, 2H, *H*-Ar), 4.24 (t, J = 6.7 Hz, 4H, OCH_2), 4.17 (t, J = 7.0 Hz, 4H, OCH_2), 3.97 (s, 4H, COCH_2CO), 2.15−1.99 (m, 8H, CH_2), 1.54−1.26 (m, 40H, CH_2), 0.86−0.83 (m, 12H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K, TMS): δ 163.0, 162.9, 161.7, 160.6, 160.3, 156.5, 133.0, 130.6, 120.6, 120.4, 113.1, 112.9, 98.0, 69.7, 68.9, 31.2, 28.7, 28.6, 28.5, 28.3, 25.5, 22.0, 13.9. IR (KBr): ν = 3316, 3208, 2926, 2858, 1626, 1466 cm^{-1}. ESI MS: *m/z* 1113.98 [M − H]$^-$. Anal. Calcd for $C_{60}H_{90}N_8O_{12}$: C, 64.61; H, 8.13; N, 10.05. Found: C, 64.39; H, 8.19; N, 10.29.

Acknowledgment. We thank the National Natural Science Foundation of China (20625206), National Basic Research Program of China (2007CB808004, 2008CB617501), and CMS-Y 200708 for financial support.

Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra for new compounds. Stacked partial ^{1}H NMR spectra for the duplex strands at different temperatures and 2D NOESY spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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