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Self-assembly and characterization of a hydrogen-bonded supramolecular system between an oligo-2-aminopyridine derivative and 1-dodecyluracil☆

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Abstract

A new self-assembled supramolecular system between an oligo-2-aminopyridine derivative and 1-dodecyluracil through hydrogen bonding interaction was designed and prepared. The hydrogen bonding interaction was confirmed by ^{1}H NMR and UV/vis titration experiments. This self-assembled system can form spherical particles, which can be observed by TEM, indicating that the complementary linear oligo-2-aminopyridine derivative and the uracil derivative can be used for the construction of three-dimensional ball-like aggregates by the hydrogen bonding interaction.

Keywords: Oligo-2-aminopyridine; Self-assembly; Hydrogen bonding interaction

1. Introduction

In recent years, considerable interest has been shown in the design and synthesis of hydrogen-bonded self-assembled supramolecular systems. Many examples of using hydrogen-bonding interactions to control the self-assembly of molecules into well-defined aggregates have been reported [1–8]. Meanwhile, energy and electron-transfer processes have also been investigated in some systems assembled through hydrogen bonding [2,3]. Multiple hydrogen bonds between complementary molecular components are popularly used as the driving force for the formation of dimers or oligomeric aggregates in the organic media. The formation of hydrogen bonds between uracil moiety and 2,6-diaminopyridine unit have been proved to be an efficient way to construct supramolecular assemblies [1,5,6].

Recently, Peng reported the systematic studies on the self-complementarity of oligo-2-aminopyridines [9–11]. Because these compounds contain an alternating proton donor/acceptor sequence, oligo-2-aminopyridines tend to dimerize to form a belt-shape zipperic dimer through hydrogen bonding interaction in solution and in solid state. In this paper, we chose complementary oligo-2-aminopyridine derivative and 1-dodecyluracil to construct new supramolecular assembly through three-point hydrogen bonding.

2. Experimental

4-Dodecyloxybenzylbromide [13] and N^2,N^6-bis(6′-bromopyridine-2′-yl)-pyridine-2,6-diamine [11] were synthesized according to the literature method.

2.1. N-(4′-Dodecyloxybenzyl)pyridine-2,6-diamine

To a mixture of 2,6-diaminopyridine (327 mg, 3 mmol) and KO-*t*Bu (672 mg, 6 mmol) in dry dioxane (10 mL) was added a solution 4-dodecyloxybenzylbromide (710 mg, 2 mmol) in dioxane (2 mL) at room temperature with constant stirring. The mixture was stirred at 100 °C for 6 h under argon. After cooling, the crude mixture was quenched with saturated NH_4Cl solution

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(2 mL), then dichloromethane (15 mL) and water (10 mL) was added. After extraction, the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed, and the crude product was chromatographed over silica gel (petroleum ether/EtOAc = 2:1) to give *N*-(4′-dodecyloxybenzyl)pyridine-2,6-diamine (437 mg, yield 57%) as a light brown solid. mp 89–90 °C; IR (KBr): 3421, 3319, 2921, 2852, 1593, 1464, 1248 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$): δ 7.19–7.24 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H), 5.84 (d, J = 8.0 Hz, 1H), 5.76 (d, J = 8.0 Hz, 1H), 4.60 (bs, 1H), 4.33 (d, J = 5.6 Hz, 2H), 4.18 (bs, 2H), 3.93 (t, J = 6.8 Hz, 2H), 1.72–1.79 (m, 2H), 1.40–1.46 (m, 2H), 1.26–1.40 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H); MS: m/z (EI, 70 eV) 383 [M^+, 37.9%].

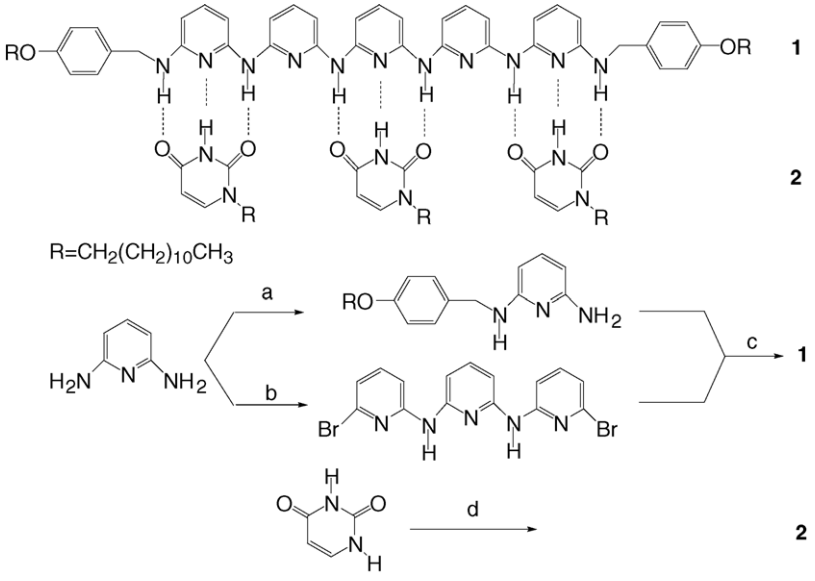
2.2. N^2,N^6-{6′-[(6″-(4‴-Dodecyloxybenzylamino)pyrid-2″-yl)amino]pyrid-2′-yl}pyridine-2,6-diamine (**1**)

The mixture of *N*-(4′-dodecyloxybenzyl)pyridine-2,6-diamine (230 mg, 0.6 mmol) and N^2,N^6-bis(6′-bromopyridine-2′yl)-pyridine-2,6-diamine (126 mg, 0.3 mmol) in the presence of $Pd_2(dba)_3$ (9.6 mg, 3 mol%), BINAP (11.4 mg, 6 mol%), KO-*t*Bu (168 mg, 1.5 mmol), and 18-crown-6 (158 mg, 0.6 mmol) in dry benzene (2 mL) was refluxed for 12 h under argon. Purification by column chromatography over silica gel(EtOAc) to give the pure product(102 mg, 33%) as a light brown solid. mp 193–194°; IR (KBr): 3420, 3198, 3016, 2924, 2853, 1578, 1428 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$): δ 11.49 (s, 2H, NH), 10.83 (bs, 2H, NH), 7.41–7.45 (m, 3H), 7.23–7.30 (m, 4H), 7.18 (s, 4H), 7.00 (bs, 2H), 6.76–6.81 (m, 8H), 6.50 (d, J = 7.6 Hz, 2H), 5.85 (d, J = 6.0 Hz, 2H), 4.27 (bs, 4H), 3.89 (t, J = 6.4 Hz, 4H), 1.3–1.8 (m, 40H), 0.88 (t, J = 6.4 Hz, 6H); ^{13}C NMR(400 MHz, $CDCl_3$): 158.1, 154.6, 154.4, 154.0, 139.3, 139.2, 139.0, 130.7, 127.9, 114.4, 103.5, 103.1, 102.8, 99.9, 97.2, 67.9, 45.9, 31.8, 29.5, 29.4, 29.3, 26.0, 22.6, 14.0; MALDI-TOF MS: Calcd. for $C_{63}H_{83}N_{11}O_2$ (M^+), m/z = 1025.7; found, 1026.9 ($M + H^+$).

3. Results and discussion

The synthesis of oligo-2-aminopyridine derivative (**1**) and 1-dodecyluracil (**2**) is illustrated in Scheme 1. Compound **1** was synthesized on the basis of the Buchwald's palladium-catalyzed amination procedures [12]. To construct the target molecule, terminal building block *N*-(4-dodecyloxybenzyl)pyridine-2,6-diamine was prepared from benzylation of 2,6-diaminopyridine by using 4-dodecyloxybenzylbromide [13]. The dodecyl group was introduced in order to enhance the solubility of **1** in organic media. The internal building block N^2,N^6-bis(6′-bromopyridine-2′-yl)-pyridine-2,6-diamine was obtained from a base-catalyzed coupling reaction by using 2:1 ratio of 2,6-dibromopyridine and 2,6-diaminopyridine [9]. The internal building block was reacted with 2 equiv. of terminal building blocks in the presence of $Pd_2(dba)_3$ (3 mol%) and BINAP (6 mol%) as the catalysts to give the target molecule **1**. 18-Crown-6 was added in order to facilitate the coupling reaction. Compound **2** was synthesized from uracil and 1-bromododecane according to the common condensation procedure [6a]. The oligo-2-aminopyridine derivative has sufficient solubility in organic solvents to be characterized by ^1H NMR spectroscopy. The spectrum shows all the signals characteristic for the formation of hydrogen bonded assembly [9].

It is well known that the characteristic of the formation of three-point hydrogen bonding complex between uracil moiety and diaminopyridine unit is the downfield shifts of their amidic protons in the supramolecular system [1,5]. The imidic proton signal of the uracil moiety undergoes a significant downfield shift of several ppm in the ^1H NMR titration experiment due to



Scheme 1. *Reaction conditions*: (a) 4-dodecyloxybenzylbromide, *t*BuOK, benzene, reflux, 10 h, 57%; (b) 2,6-dibromopyridine, *t*BuOK, dioxane, reflux, 10 h, 23%; (c) *t*BuOK, 18-crown-6, $Pd_2(dba)_3$, BINAP, benzene, reflux, 10 h, 33.2%; (d) 1-bromododecane, DMSO, 40°, 24 h, 70%.