BIOMACROMOLECULES

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Selective Gas Capture Ability of Gas-Adsorbent-Incorporated Cellulose Nanofiber Films

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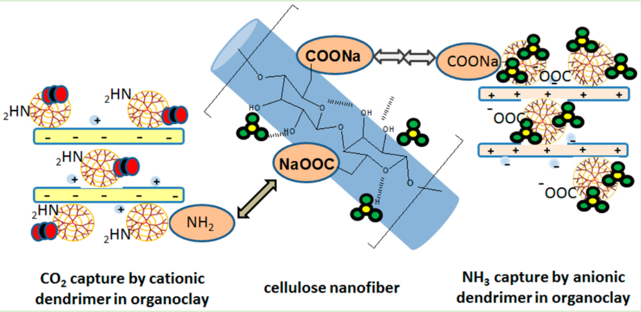
Ⓢ *Supporting Information*



ABSTRACT: The 2,2,6,6-tetramethylpiperidine-1-oxyl radical-oxidized cellulose nanofibers (TOCNF) were hybridized with cation and anion-exchange organoclays, where poly(amido amine) dendrimers were loaded to enhance the functionality of gas adsorption, since dendrimers have the high adsorbability and the enough selectivity on the gas adsorption. The thin films were prepared from the organoclay-TOCNF hybrids and supplied to the gas adsorption. The adsorption of CO$_2$ and NH$_3$ gases increased with an increasing amount of organoclays in TOCNF films, but the behavior of the increase depended on gases, clays, and dendrimers. The hydrotalcite organoclay-TOCNF films displayed the highest adsorption of both gases, but the desorption of CO$_2$ gas from hydrotalcite organoclay-TOCNF films was drastically high in comparison with the other systems. While the CO$_2$ gas is adsorbed and remained on cationic dendrimer sites in cation-exchange organoclay-TOCNF films, the CO$_2$ gas is adsorbed on cationic clay sites in anion exchange organoclay-TOCNF films, and it is easily desorbed from the films. The NH$_3$ adsorption is inversive to the CO$_2$ adsorption. Then the CO$_2$ molecules adsorbed on the cationic dendrimers and the NH$_3$ molecules adsorbed on the anionic dendrimers are preferably captured in these adsorbents. The present research incorporated dendrimers will be contributing to the development of gas-specialized adsorbents, which are selectively storable only in particular gases.

1. INTRODUCTION

The most serious environmental issue should be climate changes and global warming caused by an increase of greenhouse gases in the atmosphere,[1−3] and more than half of global warming may be caused by CO$_2$ gas alone.[4] The CO$_2$ gas is mainly emitted from the industries, which is one of the major sources on the emission of greenhouse gases. Meanwhile, nitrogenous gases are released from agricultural wastes,[5−7] and NH$_3$ gas is major among various nitrogenous gases. To control the greenhouse gases, many gas-adsorbing materials have been developed and used worldwide.[4] Among gas adsorbents, functional nanomaterials such as carbon, metal, and semiconductor have been limited in use due to their too small sizes and toxicity.[8] Thus, adequate supporting scaffolds are a great interest for holding these adsorbents.

Since the cellulose is a prevalent biopolymer and possesses a biodegradable nature, it has been applied to adsorption of polluted gases.[9−13] However, the presence of multiple hydrogen bonds between cellulose fibers in the plant is a major difficulty on the surface modification of fibers.[14] Thus, the chemical treatment has been attempted to obtain the nanofiber of cellulose. Among many chemical treatments, the oxidation reaction mediated by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical is adopted in acquiring the fiber of nanometer thickness without the break of the length.[15−17] Moreover, to improve properties and functionalities of cellulose fiber, inorganic particles have been incorporated.[18−20] Among them, clay is an environmentally friendly material and was taken in cellulose nanofibers (CNF) to improve properties such as modulus, strength, and toughness.[21−24] Moreover, TEMPO-oxidized CNF (TOCNF) can form transparent films, and metal-embedded TOCNF films presented the renewable catalytic efficiency and the excellent antibacterial performance.[25,26]

The present study explored the adsorption of CO$_2$ and NH$_3$ gases on the hybridized films of TOCNF with organoclays. To the best of our knowledge, this is the first report that focuses on organoclays embedded into the TOCNF film for gas adsorption. Compared with pristine clays, organoclays loading functional organic molecules like dendrimers are favorable for gas adsorption;[27,28] Dendrimer moieties possess highly functional terminal groups and can become the binding site adaptable to the adsorption of gases. On the preparation of gas adsorbents, cationic and anionic dendrimers were selected as modifiers of cation-exchange (laponite and sericite) and anion-exchange (hydrotalcite) clays, respectively. These clays and dendrimers provide adequate binding sites besides a binding site of TOCNF during

Received: January 15, 2016
Revised: March 31, 2016
Published: April 1, 2016

DOI: 10.1021/acs.biomac.6b00065
Biomacromolecules 2016, 17, 1653−1661

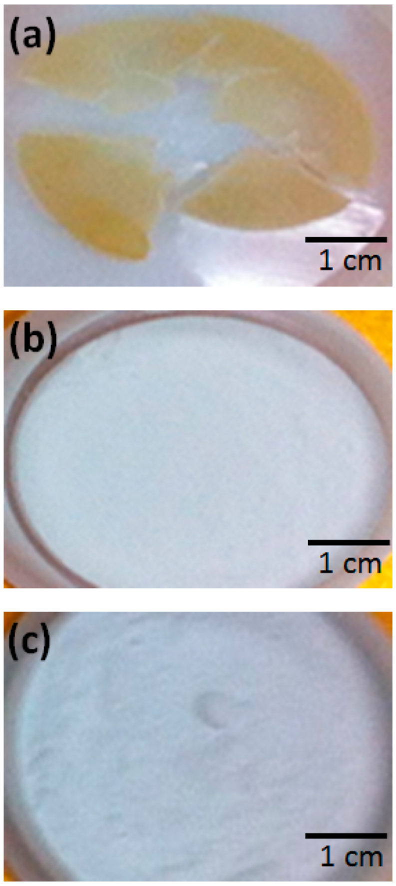


Figure 1. Photographs of clay0.5-TOCNF films at 5.0 g/g(TOCNF): (a) laponite, (b) sericite, and (c) hydrotalcite.

the gas adsorption. Therefore, the selectivity of organoclay-embedded TOCNF on the CO_2 and NH_3 gas adsorption is the major focus of this research. For the assessment of the clay in TOCNF, the films were characterized, and adsorption–desorption studies of gases were carried out. The behaviors of adsorption and desorption were compared among all TOCNF films incorporated cation- and anion-exchange organoclays.

2. EXPERIMENTAL SECTION

2.1. Materials. Abies sliced wood (softwood) and TEMPO free radical were obtained from Canary Corporation and Acros organics, respectively. Laponite (a XLG grade) and hydrotalcite clays were purchased from Southern Clay Products and Wako Chemicals, respectively. Sericite (a FSN grade) clay was donated from Sanshin Mining Ind. Co. Ltd. Amine-terminated fourth generation (G4.0) poly(amido amine) (PAMAM) dendrimer (MW 14213) and carboxylate-terminated G4.5 PAMAM dendrimer (MW 26258) were purchased from Sigma-Aldrich. Ultrapure water (resistivity of 18.2 MΩ·cm) was obtained from a Yamato Millipore WT100. All other commercially available chemicals were of analytical grade and used without further purification.

2.2. Preparation of TOCNF. TOCNF was prepared as below.[15,17] First, softwood was dewaxed by refluxing with a toluene/ethanol (2:1 by volume) mixture for 8 h in a Soxhlet extractor. According to the Wise's method,[29] the dewaxed wood was delignified by the treatment with a sodium chlorite ($NaClO_2$) solution for 1 h at pH 4−5 (maintained by adding acetic acid) and 80 °C. After this process was repeated several times, the product was rinsed with water and kept wet as a never-dried pulp.

Second, the never-dried pulp was oxidized to prepare nanofiber.[30] The diluted never-dried pulp (1 wt %) in water (100 mL) added sodium bromide (0.1 g) and TEMPO (0.016 g) under continuous stirring was further added sodium hypochlorite (NaClO, 13 vol %) to initiate the reaction. The slurry was stirred at room temperature and pH 10, which should be adjusted by 0.1 M HCl or 0.5 M NaOH through the reaction. After the pH of the slurry remained unchanged, the oxidized pulp was filtrated and rinsed until the pH of the filtrate became 7. The obtained TEMPO-oxidized cellulose pulp with sodium carboxylate groups (TOCF-COONa) was reduced by adding sodium borohydride ($NaBH_4$, 1 g) with stirring for 8 h and the reduced TOCF-COONa was thoroughly rinsed with water by centrifugation. The nanofibrillation to form nanofiber (TOCNF-COONa) was performed by ultrasonicating the slurry of reduced TOCF-COONa (0.1 wt %) in water for 40 min at 20 amplitude with an ultrasonic processor (QSONICA Q700) with a half-inch tip. During the sonication, the slurry was kept cooled by the ice bath to minimize overheating.

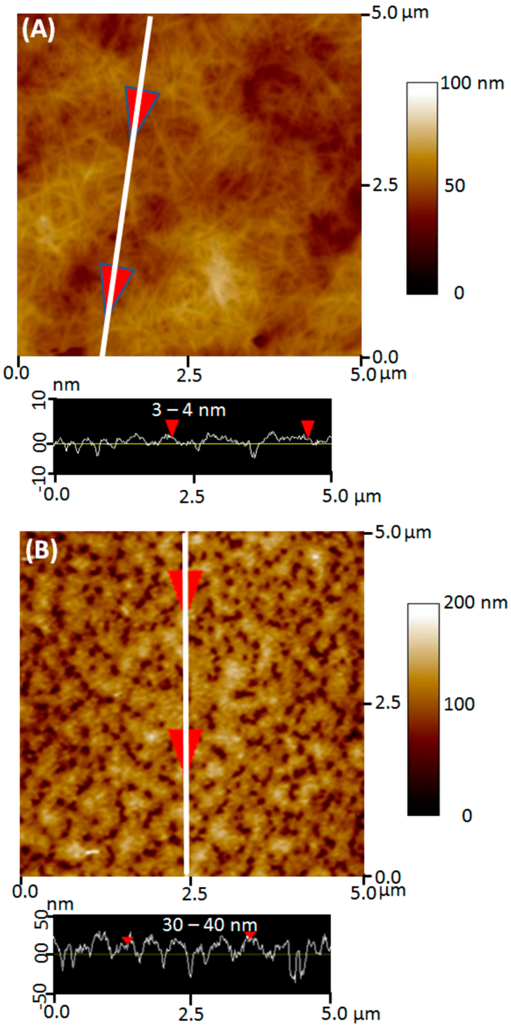


Figure 2. AFM images and section analyses of (A) TOCNF film and (B) Lap0.5-TOCNF film at 0.1 g/g(TOCNF).

2.3. Preparation of Clay- and Organoclay-TOCNF Films. Following previous reports,[27,31−33] organoclays were prepared by the ion-exchange process at acidic pH. In practice, clay and dendrimer was stirred in water for 2 days at pH 4 and 70 °C to obtain the maximum intercalation of dendrimer into clay, purified by centrifugation, and dried in vacuum for 6 h. Amine-terminated G4.0 PAMAM dendrimer was used for the reaction with laponite and sericite, and carboxylate-terminated G4.5 PAMAM dendrimer was reacted with hydrotalcite.

Clay- and organoclay-TOCNF films, respectively, with three clays (clay0.0: Lap0.0, Ser0.0, and Hyd0.0, where 0.0 means the zero proportion of dendrimer) and corresponding organoclays (organoclay0.5: Lap0.5, Ser0.5, and Hyd0.5, where 0.5 indicates the weight proportion of dendrimer against clay) were prepared by the vacuum drying process.

DOI: 10.1021/acs.biomac.6b00065
Biomacromolecules 2016, 17, 1653−1661

Table 1. Contact Angle, BET Surface Area, BJH Pore Size, and Pore Volume of TOCNF Film and Clay-TOCNF Films of Clay0.0 and Organoclay0.5 at 0.25 and 0.50 g/g(TOCNF)

	contact angle (degree)			surface area (m^2/g)			pore size (nm)			pore volume (cm^3/g)		
TOCNF film	18			10			1.8			0.025		
clay-TOCNF film	Lap	Ser	Hyd	Lap	Ser	Hyd	Lap	Ser	Hyd	Lap	Ser	Hyd
0.25 g/g(TOCNF)												
clay0.0	40	28	26	3.6	9.2	24.2	1.8	5.1	6.2	0.082	0.068	0.540
clay0.5	48	32	24	1. 2	11.7	32.4	2.3	5.4	6.5	0.026	0.045	0.295
0.50 g/g(TOCNF)												
clay0.0	50	32	22	11.5	13.0	44.7	2.0	6.0	7.1	0.090	0.078	0.606
clay0.5	56	36	20	8.6	11.1	34.5	2.5	6.2	7.5	0.036	0.048	0.310
Clay[a]												
clay0.0	80	66	44	358	11.7	46.0	2.8	10.5	18.9	0.252	0.133	0.650
clay0.5	81	67	36	55	13.2	58.0	4.0	11.6	20.3	0.098	0.068	0.547

[a] Clay pellets were prepared by tightly packing in a powder-press instrument.

Briefly, an aqueous 10 wt % TOCNF-COONa dispersion was sonicated for 30 min and mixed with a clay or organoclay dispersion (50 wt % in water), and the mixture was vigorously stirred 1 h at room temperature. Then the mixture poured into the polystyrene Petri dish was vacuum-dried for 3 days at 40 °C to obtain the clay- or organoclay-TOCNF film, and the film was carefully peeled off from the Petri dish. Finally, clay- and organoclay-TOCNF films with different clay or organoclay ratios (up to 5 g/g(TOCNF)) were obtained. The TOCNF-COONa film without clay and organoclay was also correspondingly prepared.

2.4. Instruments and Measurements. An atomic force microscopic (AFM) observation was carried out on a Digital Instrument Nanoscope III (Veeco) at contact mode. Contact angle was measured on a UPG620 USB digital camera (UPMOST Technology Corp., Taiwan). An N_2 adsorption−desorption isotherm was measured on a Brunauer−Emmett−Teller (BET) isotherm measurement instrument (BELSORP-max, BEL, Japan, and NOVA 1000e surface area analyzer). Before going for the N_2 adsorption−desorption, clay- or organoclay-TOCNF without NH_3 or CO_2 adsorption were pretreated in a vacuum chamber at 50 °C for 3 h and supplied for the N_2 adsorption−desorption measurements. Clay- or organoclay-TOCNF adsorbed NH_3 or CO_2 gas was directly provided for N_2 adsorption−desorption studies to avoid loss of the adsorbed gas. The surface area was calculated from obtained adsorption−desorption isotherm curve along a Brunauer−Emmett−Teller (BET) surface area analysis.

Following the previous report,[27] the adsorption experiment of CO_2 for all clay- and organoclay-TOCNF films was carried out for 300 min at room temperature on a TGA instrument (Q500 TA) with N_2 gas flow (balance chamber) and CO_2 (pure) gas flow (sample chamber) with flow rates of 40 and 60 mL·min^{-1}, respectively. NH_3 gas adsorption was performed on the specially designed adsorption system (Supporting Information, Figure S1). The ammonium hydroxide solution in chamber was heated to generate NH_3 gas and the amount of gas adsorption was gravimetrically measured. Desorption experiments were carried out first by removing the moisture under N_2 atmosphere as pretreatment for adsorption−desorption experiments. Then, after adsorbing CO_2 or NH_3 for 100 min at room temperature, desorption experiments were performed for 200 min at 40 °C under the flow of N_2 gas.

3. RESULTS AND DISCUSSION

3.1. Characterization of Organoclay-TOCNF Hybrid Films. Nanofiber of TEMPO-oxidized cellulose (TOCNF-COONa) was prepared, and pristine clays or dendrimer-loaded organoclays were embedded in TOCNF-COONa to form clay- or organoclay-TOCNF hybrid films at different mixing ratios (g/g(TOCNF)) of clay0.0 and clay0.5. While the plain TOCNF film prepared from only TOCNF-COONa was transparent without color, the hybrid films of sericite and hydrotalcite were whitened, although the hybrid film of laponite was pale brown and breakable at the mixing ratios of higher than 3.0 g/g(TOCNF), as shown in Figure 1. The film (0.1 g/g(TOCNF)) of Lap0.5-TOCNF-COONa was characterized by AFM and compared with the film of TOCNF-COONa. The AFM image showed that the surface of the TOCNF film consists of randomly assembled fine fibers (Figure 2A). On the other hand, the AFM image of the Lap0.5-TOCNF hybrid film presented the homogeneous texture with about 30−40 nm roughness, as seen in Figure 2B. The similar texture was also displayed by the Lap0.0-TOCNF hybrid film (the image is not shown.). These textures confirm that clays and organoclays are certainly incorporated and uniformly distributed in the TOCNF film.

The difference of the clay- and organoclay-TOCNF hybrid films from the TOCNF film on AFM texture may affect the contact angle and BET adsorption behavior of the films. The contact angles of the TOCNF film and the TOCNF hybrid films prepared at different mixing ratios of pristine clays and organoclays are listed in Table 1, which also includes the contact angles of pristine clay and organoclay pellets. The TOCNF film had a contact angle of 18°, and it increased at the embedding of clays due to the hydrophobic nature of clay, as known from the contact angle values of pristine clay pellets. As seen in Figure 3A, contact angles of clay-TOCNF hybrid films were increased with increasing the organoclay content for the cation-exchange clays (laponite and sericite), but they were decreased for the anion-exchange clay (hydrotalcite). The increase of contact angle for Lap0.5-TOCNF and Ser0.5-TOCNF films was nearly 4× and 3×, respectively, superior to the pristine TOCNF film, while such drastic increment of the contact angle could not occur on Hyd0.5-TOCNF films and rather the contact angle decreased with organoclay content. This is due to the neutralization of a carboxylate moiety on TOCNF by amine-terminated dendrimer to become hydrophobic for the cases of laponite and sericite and the increase of hydrophilic carboxylate moiety from COONa-terminated dendrimer to increase hydrophilicity for the case of hydrotalcite. These results indicate that the hydrophobicity of organoclay-TOCNF films is highest for laponite and lowest for hydrotalcite.

The N_2 adsorption−desorption isotherms of clay0.5-TOCNF films at different weight ratios of organoclay were measured and compared with those of clay0.5 powders, as shown in Figure 4. Types of isotherms were assigned, according to the BDDT classification from IUPAC.[34] Laponite and hydrotalcite organoclays displayed mesoporous IV-H2 and nonporous-III isotherms, respectively. After the incorporation of 0.5 and 5.0 g/g(TOCNF)

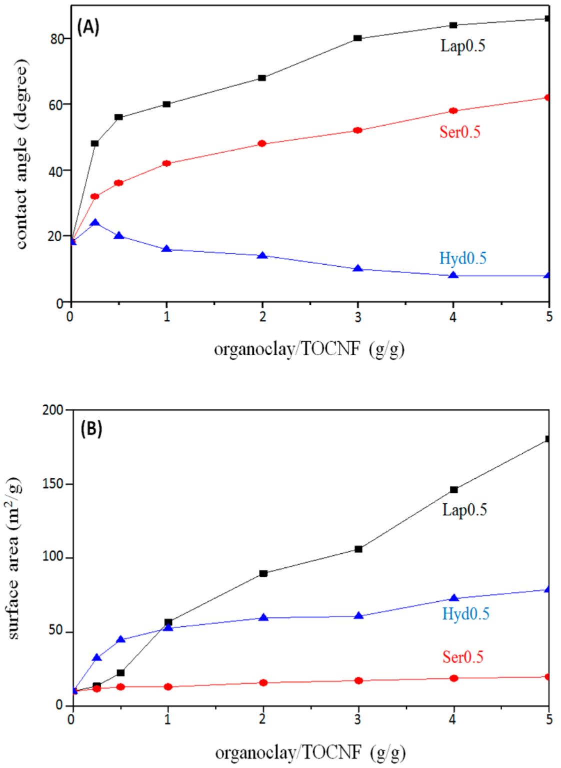


Figure 3. (A) Contact angle and (B) BET surface area of clay0.5-TOCNF films as a function of organoclay content in TOCNF film.

organoclays in TOCNF films, characteristics of isotherms were changed to nonporous-II and nonporous-III, respectively, for laponite organoclay and kept the same type for hydrotalcite organoclay. The difference in types should depend on the available volume of clays, as seen in Figure 4, and will be reflected in the characteristics of clays. Moreover, when the large amount of organoclays was embedded in TOCNF films, the characteristics of isotherms of organoclay-TOCNF films approach to it of organoclays alone. This tendency suggests the effect of clay content on the surface characteristics of the films.

Table 2 also lists the BET surface areas of the TOCNF film and the TOCNF hybrid films at different mixing ratios of clays and organoclays on films along with the pristine clay and organoclay pellets. The surface areas are also plotted in Figure 3B as a function of organoclay content. When the organoclay content was increased, the surface area of TOCNF hybrid films increased for all three organoclays, although the order of laponite > hydrotalcite > sericite was different from that of the contact angle. Differently from the fact that the contact angle is affected by the hydrophobicity of the films, the surface area of the films may depend on other factors like the size of fillers. Incidentally, the particle size of organoclay relating to the dendrimer loading amount was the order of laponite < hydrotalcite < sericite.[27]

3.2. Adsorption−Desorption of CO_2 and NH_3 Gases on Organoclay TOCNF Hybrid Films. The CO_2 adsorption on clay0.5-TOCNF films at different embedding contents of organoclays is shown in Figure 5. In common, after the films were exposed to CO_2 gas, the CO_2 adsorption started and increased, involving slowdown, although the adsorption at high organoclay content did not reach the saturation even after the reaction time of 300 min. The CO_2 adsorption of the clay0.5-TOCNF film at 0.25 g/g(TOCNF) was always higher than that of the clay0.0-TOCNF film, and the CO_2 adsorption of the TOCNF film without organoclay was lowest. These results indicate that CO_2 adsorbed on clay and dendimer but less on TOCNF.

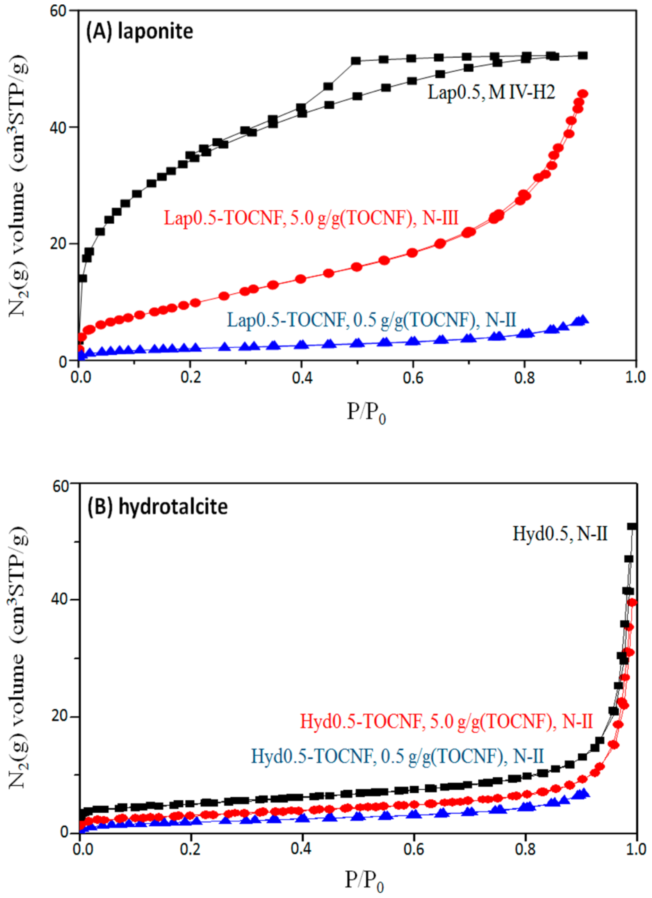


Figure 4. Nitrogen gas adsorption−desorption isotherms of clay0.5 and clay0.5-TOCNF films at 0.5 and 5.0 g/g(TOCNF).

Table 2. BET Surface Area, BJH Pore Size, and Pore Volume of TOCNF Hybrid Films of Lap0.1 and Hyd0.1 at 0.5 and 5.0 g/g(TOCNF)

	surface area (m^2/g)	pore size (nm)	pore volume (cm^3/g)
Lap0.1, 0.5 g/g(TOCNF)	12	2.5	0.030
Lap0.1, 5.0 g/g(TOCNF)	160	3.0	0.086
Lap0.1	285	3.4	0.112
Hyd0.1, 0.5 g/g(TOCNF)	32.6	7.5	0.360
Hyd0.1, 5.0 g/g(TOCNF)	39.5	14.8	0.520
Hyd0.1	48.3	19.5	0.575

The CO_2 adsorption of the clay0.5-TOCNF films at 300 min reaction is plotted in Figure 6(A) as a function of organoclay content. The adsorption increased with increasing the organoclay content. The Hyd0.5-TOCNF film displayed the highest CO_2 adsorption, and the CO_2 absorption of the Lap0.5-TOCNF film was higher than that of the Ser0.5-TOCNF film. This order is consistent with it of surface area but not of contact angle. This suggests that CO_2 adsorption is not affected by only types (cation-exchange or anion-exchange) of organoclays, but other factors like surface area or particle size influence on the adsorption property.

The NH_3 adsorption of the clay0.5-TOCNF films at different organoclay contents was measured under humid NH_3 atmosphere.

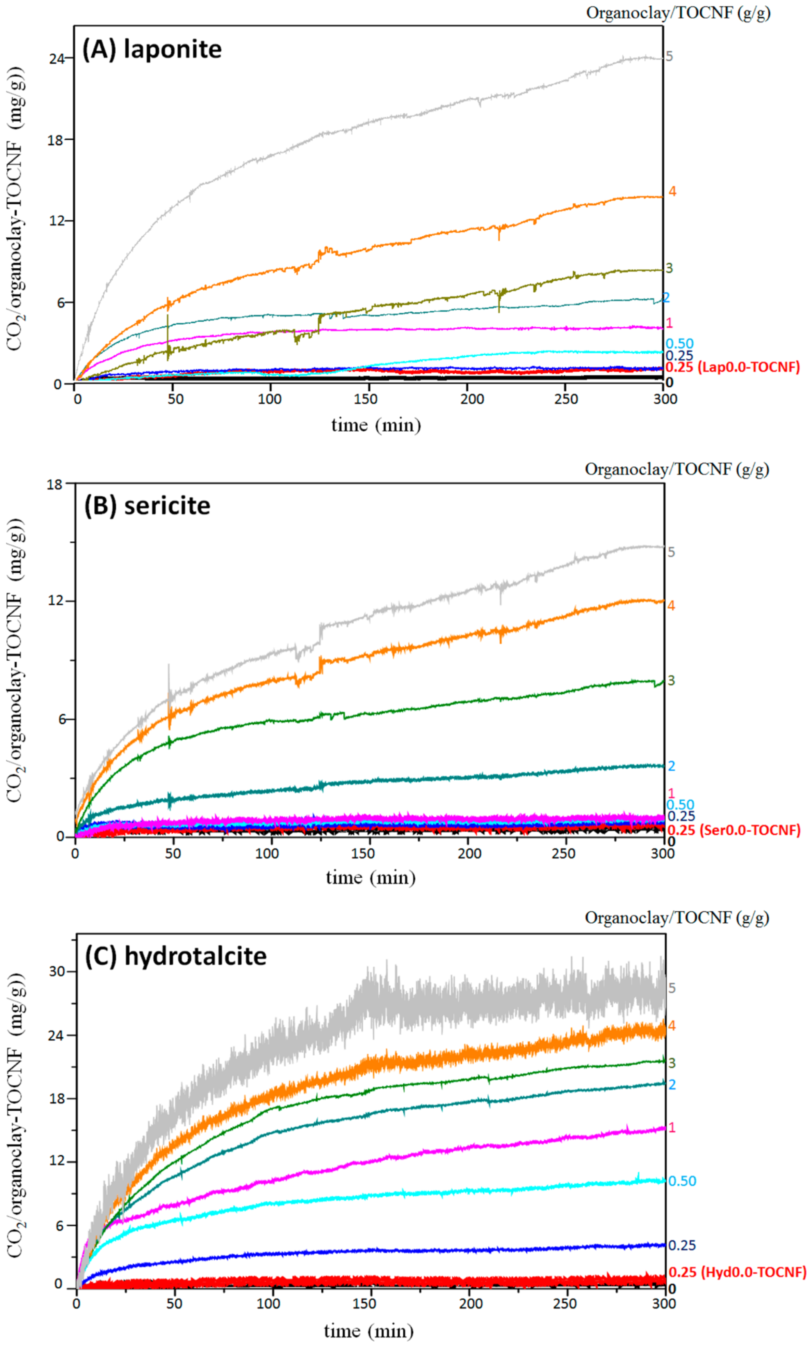


Figure 5. Time-dependent CO_2 adsorption on clay0.5-TOCNF films at different organoclay contents: (A) laponite, (B) sericite, and (C) hydrotalcite. Data on clay0.0-TOCNF films at 0.25 g/g(TOCNF) are also included.

The NH_3 adsorption at 300 min reaction is plotted in Figure 6B as a function of organoclay content in the TOCNF films. Although the adsorption of H_2O vapor was also measured, it was negligibly low (only 1 mg/g(TOCNF)). The TOCNF film without organoclay adsorbed NH_3 gas of around 9–10 mg/g(TOCNF). This amount was higher than the adsorption (below 2.5 mg/g(TOCNF)) of CO_2 gas (Figure 6A), because the COONa moiety in TOCNF has high affinity toward NH_3 gas unlike CO_2 gas.[27] Moreover, the NH_3 adsorption increased with increasing organoclay content for all three clays alike CO_2 gas. The Hyd0.5-TOCNF film was indicative of the highest NH_3 adsorption, and the Ser0.5-TOCNF film exhibited the second-highest NH_3 absorption. Moreover, the NH_3 adsorption of the Hyd0.5- and Ser0.5-TOCNF films was almost double of the CO_2 adsorption but it of Lap0.5-TOCNF film was similar to the CO_2 adsorption.

To confirm the storage (residual) of gases, desorption experiments were performed on organoclay-TOCNF films. The adsorbed, desorbed, and residual (after the desorption) amounts of CO_2 on clay0.5-TOCNF films were plotted in Figure 7 (left) as a function of organoclay content. Many of adsorbed CO_2 molecules were desorbed from the Hyd0.5-TOCNF films, but they remained in the Lap0.5-TOCNF films. Similar behavior has been observed on laponite organoclay without TOCNF, where the captured CO_2 was fixable on amine-terminated dendrimer.[27] This suggests that CO_2 molecules adsorbed on TOCNF were easy released, but CO_2 molecules adsorbed on embedded cation-exchange organoclays (laponite and sericite) were mostly

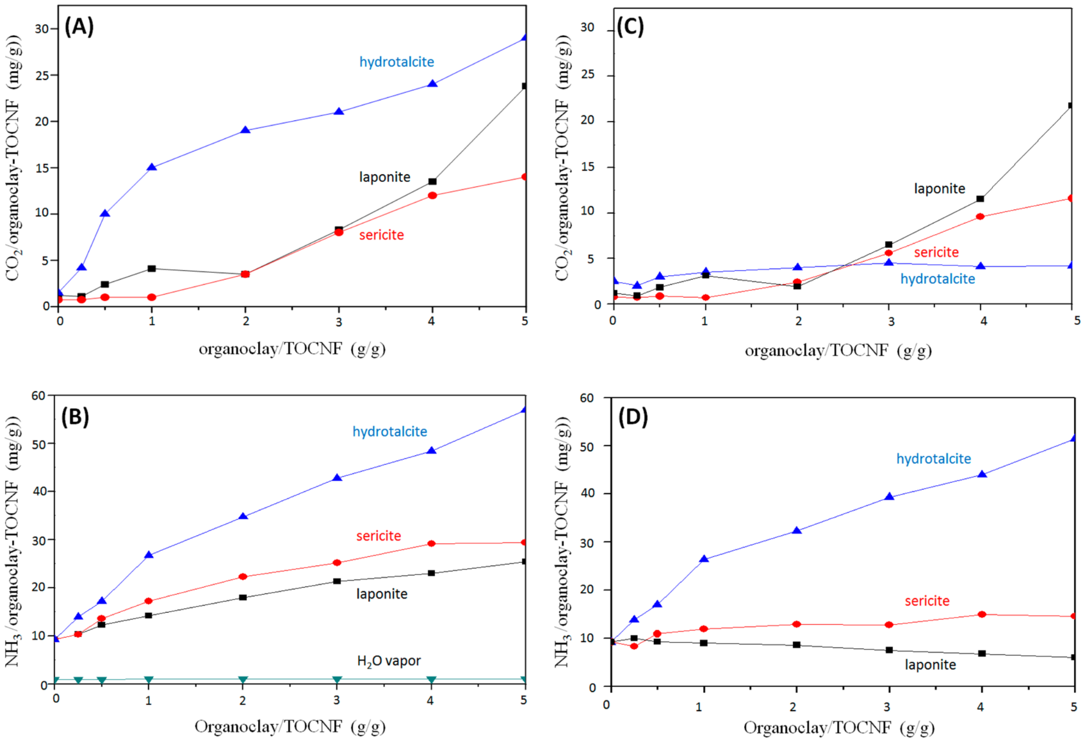


Figure 6. (A) CO_2 and (B) NH_3 adsorption on clay0.5-TOCNF films as a function of organoclay content in TOCNF film: (C) stored CO_2 and (D) stored NH_3 obtained in Figure 7.

remained. Contrarily, despite the highest CO_2 gas adsorption among three clays on organoclay-TOCNF films, many CO_2 gas molecules were desorbed from Hyd0.5-TOCNF films, indicating the absence of active storage sites for CO_2 gas.

By comparison with the CO_2 desorption, the NH_3 desorption was performed on clay0.5-TOCNF films. In Figure 7 (right), the NH_3 desorption was compared with the adsorption and the difference as a function of organoclay content. A part of adsorbed NH_3 molecules was desorbed from the Lap0.5- and Ser0.5-TOCNF films, but a few of them was released from the Hyd0.5-TOCNF films. These behaviors of the NH_3 desorption were completely opposite of the cases of the CO_2 desorption described above. The residual, namely, stored CO_2 and NH_3 gases are plotted in Figure 6C and D, respectively. The order of the stored CO_2 of laponite > sericite > hydrotalcite was the same as the order of CO_2 adsorption on free organoclays,[27] and the inverse order of NH_3 gas adsorption (laponite < sericite < hydrotalcite) indicates the completely different affinities of adsorption sites of NH_3 gas with CO_2 gas.

3.3. Mechanism of Adsorption–Desorption of CO_2 and NH_3 Gases on Organoclay-TOCNF Hybrid Films.

Since organoclay-TOCNF hybrid films have at least three main binding sites, that is, TOCNF, clay, and dendrimer, the adsorption–desorption behaviors of CO_2 and NH_3 gases can be ascertained by the binding on individual sites. As seen in Figure 7, the CO_2 adsorption of the TOCNF film without organoclays (at 0 g/g(TOCNF)) was slight and the adsorbed CO_2 was not desorbed. The NH_3 gas was adsorbed more amount than CO_2 on the organoclay-free TOCNF film and it was not desorbed as well. These results prove the less affinity of CO_2 gas and the slight affinity of NH_3 gas to the TOCNF site but the adsorbed molecules are preserved even after the desorption procedure. The latter slight affinity may be due to the interaction of basic NH_3 molecule with the remaining anionic carboxylate moiety in TOCNF.

Amine-terminated dendrimer has specific affinity with CO_2 gas, but carboxylate-terminated dendrimer does not have such specificity.[27,28] Such features were also obtained even from the present adsorption and desorption experiments of CO_2 gas on organoclay-TOCNF films (see Figure 7 (left)): The CO_2 adsorption of Lap0.5- and Ser0.5-TOCNF films increased with increasing organoclay content but most of adsorbed CO_2 molecules were not desorbed, indicating the specific affinity of CO_2 to cation-exchange organoclays. Meanwhile, Hyd0.5-TOCNF films adsorbed CO_2 superior to other clay0.5-TOCNF films, but most of CO_2 were desorbed because of less affinity of CO_2 to anion-exchange organoclays. The former affinity should be with an amine-terminated PAMAM dendrimer site but not with the clay site itself, because acidic CO_2 has a specific interaction with cationic amine moiety, but acidic CO_2 does not adsorb on anionic clay or can be easily desorbed from clay.[27,28] Then, the abundant acidic CO_2 adsorption of Hyd0.5-TOCNF films may come from the adsorption on cationic clay site but not on anionic dendrimer site.

The situation was opposite on the adsorption and desorption of NH_3 gas on clay0.5-TOCNF films: NH_3 molecules abundantly adsorbed on Hyd0.5-TOCNF films remained even after the desorption, since basic NH_3 molecules can be strongly bound on an anionic carboxylate-terminated dendrimer site but not a cationic clay site in anion-exchange organoclay-TOCNF films. However, in the case of Lap0.5- and Ser0.5-TOCNF films, the desorption occurred parallel to the adsorption, and therefore, the remaining amount of NH_3 molecules are almost independent to the organoclay content, being indicative of basic NH_3 molecules bound on anionic clay site but not on the cationic dendrimer site, although NH_3 molecules bound on clay site are easily removed because of the nonspecific or weak

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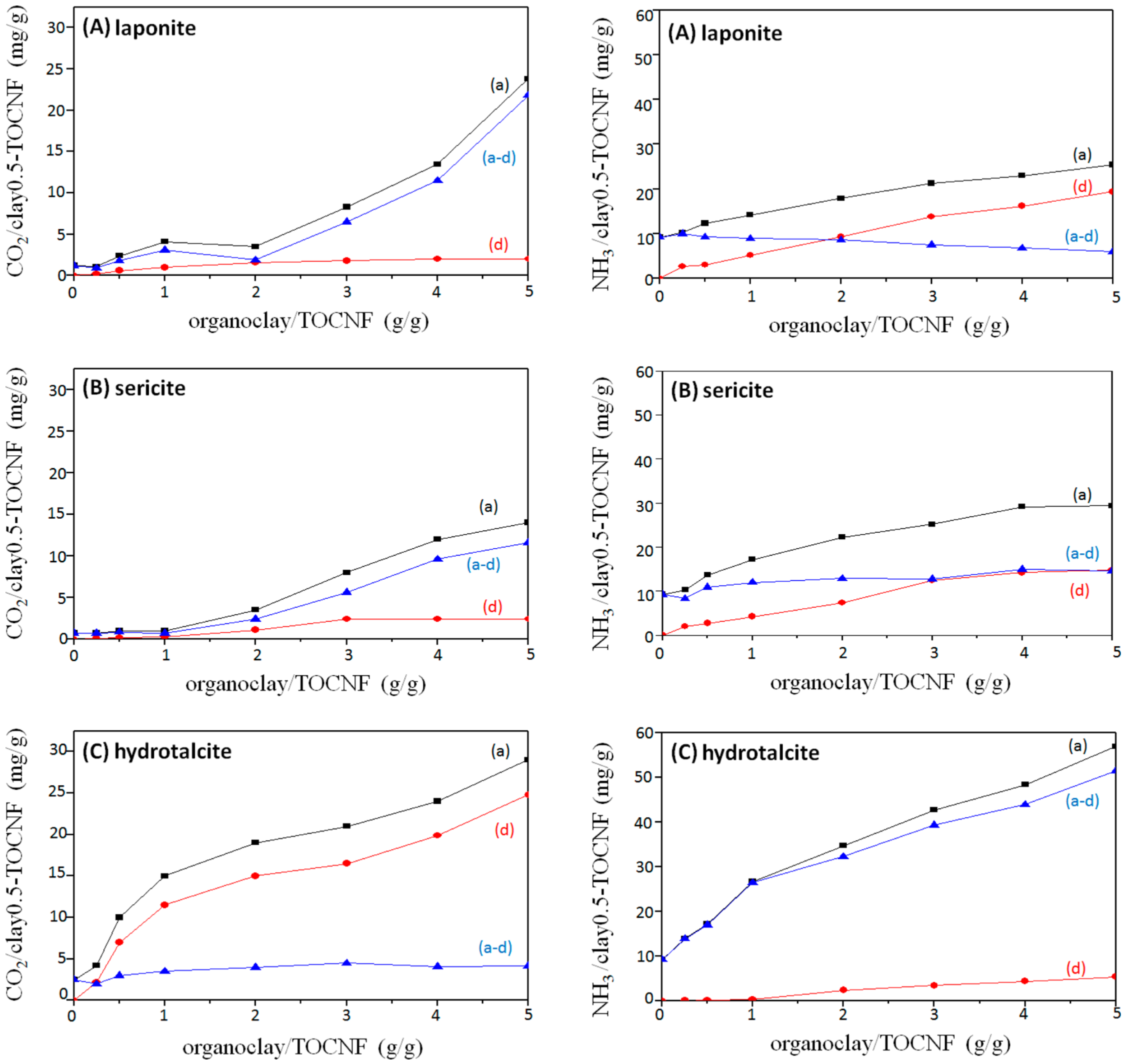


Figure 7. Plots of CO_2 (left) and NH_3 (right) gas on clay0.5-TOCNF films as a function of organoclay content in TOCNF film: (A) laponite; (B) sericite, and (C) hydrotelcite; (a) adsorbed, (d) desorbed, and (a–d) residual.

interaction. This is reasonable if NH_3 molecules have specific affinity on carboxylate-terminated dendrimer but not on amine-terminated dendrimer in inverse to the affinity of CO_2.

It should be now noticed that independent of the specific affinity of gases to dendrimers, overall adsorption of gases on organoclay-TOCNF films was always higher on anion-exchange clay systems than on cation-exchange clay systems. It may concern the contact angle of the organoclay-TOCNF films (see Figure 3A), namely, CO_2 and NH_3 gases are familiar to hydrophilic film because of their hydrophilic character to produce carboxylic ion and ammonium ion, respectively.

Based on the results obtained in this investigation, the aspect of gases adsorbed on organoclay-TOCNF films was summarized in Table 3 and illustrated in Scheme 1. The CO_2 molecules are preferably adsorbed on cationic dendrimer and clay sites and the NH_3 molecules prefer to bind on anionic dendrimer, clay and TOCNF sites. Gas molecules adsorbed on clay are easy desorbed and the amount of NH_3 adsorption on TOCNF is lower than on dendrimer. Thus, it should be noted that the cationic dendrimer and anionic dendrimer binding sites are preferable for the CO_2 and NH_3 storage, respectively.

Table 3. Aspect of Gases Adsorption on Organoclay-TOCNF Films

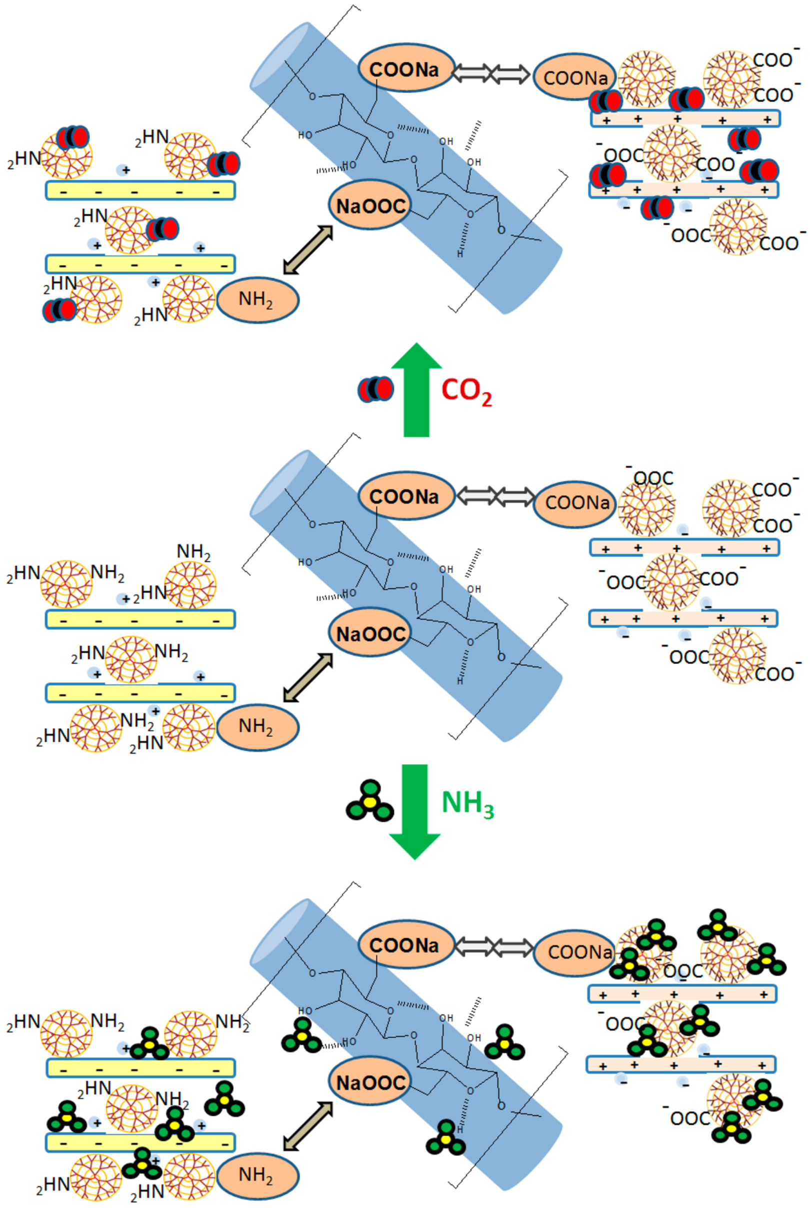
adsorbed gas	CO_2		NH_3	
TOCNF film	cation exchange	anion exchange	cation exchange	anion exchange
Binding Site				
anionic TOCNF	less	less	slight	slight
clay	(anion) less	(cation) abundant	(anion) abundant	(cation) less
dendrimer	(cation) abundant	(anion) slight	(cation) slight	(anion) abundant

4. CONCLUSIONS

In this work, the biodegradable CNF oxidized by TEMPO was functionalized to retain the adsorbents for gas molecules due to their powdery states. Although inorganic particles such as clay were useful for gas adsorption, their efficiency was still low, while organoclays containing dendrimers have preferably heightened the efficiency.[27] Therefore, in this investigation, organoclays was incorporated in the TOCNF films.

On the adsorption of CO_2 and NH_3 gases on the organoclay-TOCNF films, although the adsorption amount of both gases

Scheme 1. Schematic Representation of CO_2 and NH_3 Gas Adsorptions on Organoclay-TOCNF Films



were highest on hydrotalcite-TOCNF films, the remaining amount of CO_2 molecules on the hybrid films was dramatically decreased after the desorption process, whereas the desorption of NH_3 molecules was less. Therefore, the analyses of the gas adsorption amount and the remaining amount of gases after the desorption on TOCNF films were performed in consideration of the binding sites of TOCNF, clay and dendrimer. The results indicated that the oxidized TOCNF binding site has an anionic carboxylate moiety and preferably adsorbs basic NH_3 molecules and remains them even after the desorption unlike acidic CO_2. Since the clay and dendrimer binding sites incorporated in the organoclays have different electric charges, their adsorption behaviors for gases are opposite: The CO_2 molecules are adsorbed on cationic dendrimers in cation-exchange organoclays and on cationic clays in anion-exchange organoclays. In reverse, the NH_3 molecules can be adsorbed on anionic clays in cation-exchange organoclays and on anionic dendrimers in anion-exchange organoclays. However, since the affinity of gases on clays is not strong enough, gases are easy remove from the clays. These results suggest that the CO_2 molecules adsorbed on the cationic dendrimers and the NH_3 molecules adsorbed on anionic dendrimers are preferably stored in these adsorbents.

In the present research, the specific affinity of gases and adsorbents was confirmed and the ability of the selective gas storage was clarified. Such ability was achieved by ionic dendrimers, which were functionalized to be cationic or anionic, but it was not attained by clays and nanofibers, although they also have an adsorption ability of gases. The present research will shed light on the development of gas-specialized adsorbents, which selectively store only particular gases.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biomac.6b00065.

A schematic representation of NH_3 gas adsorption system (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by National Taiwan University of Science and Technology, Taiwan, under Grant Number 100H451201. K.S. appreciates the financial support from National Taiwan University of Science and Technology, Taiwan, for student scholarship. The authors gratefully thank Prof. M. Ujihara, National Taiwan University of Science and Technology, Taiwan, for his technical support. We appreciate Prof. A. D. Shukla, Dharmsinh Desai University, India, for his kind permission of the BET measurement.

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DOI: 10.1021/acs.biomac.6b00065
Biomacromolecules 2016, 17, 1653−1661