ACS Macro Letters

Letter

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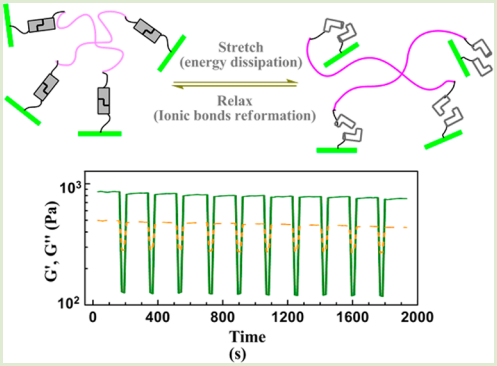
Modulation of Assembly and Dynamics in Colloidal Hydrogels via Ionic Bridge from Cellulose Nanofibrils and Poly(ethylene glycol)

Jun Yang,* Xueming Zhang, Mingguo Ma, and Feng Xu

Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, 100083, China

Supporting Information

ABSTRACT: The biologically inspired dynamic materials offer principles for designing man-made systems by using assembly approach. In this work, the hybrid hydrogels consist of cellulose nanofibrils (CNFs) that combine a mechanically strong skeleton with flexible PEG chains. The distinct gel state is observed at room temperature with $G' > G''$ and an order of magnitude higher G' values from 0.08 to 0.93 kPa upon increasing CNF concentration from 0.2 to 2 wt % at constant 2 wt % PEG. Combined with mechanically strong CNFs and dynamic ionic bridges through amine-terminated tetra-arm PEG adsorption to TEMPO-oxidized colloidal nanofibrils surface, the assembled colloidal hydrogels show high modulus, reversible gel−sol transition, and rapid self-recovery properties. It is envisioned that simply mixing hard CNF and soft polymeric matrix would lead to a facile method to bridge reversible dynamic bonds in a cellulose-based hybrid network and broad cellulose applications in the preparation of high performance supramolecular systems.



The functionalities of natural structure materials with well-defined hierarchical arrangements and the ability to dynamically interact with surrounding environment inspire us to decipher the intricate mechanisms that endow their unique properties.[1−3] Indeed, a unique aspect of most biological composites is the combination of "soft" and "hard" ingredients into complex architecture to build structures with outstanding mechanical properties.[4,5] Given many functional groups can participate in transient physical interactions, including hydrogen bonds,[6] ionic interactions,[7] metal coordination,[8] and hydrophobic association,[9] the key feature of self-recoverable materials is the ability of dynamic interactions to undergo reversible bond breaking−reformation transitions and adapt to the surrounding environment thereby.[10] It has been shown that many biological composites possess reversible sacrificial bonds that increase the energy required to break the materials.[11]

Understanding the role of dynamics and structure mechanisms in an associative polymeric gel is critical for designing soft materials.[12,13] Whereas the preparation of most supramolecular hydrogels generally relies on cyclic heating/cooling process, in situ polymerization, or cross-linking reaction, the idea of achievement of dynamic hydrogels by mixing the components in aqueous solution at room temperature is highly desirable.[14,15] Natural materials provide prototypes for outstanding mechanical properties using recyclable materials, and cellulose is a typical example that involves subtle combination of assemblies with hierarchical structure.[16,17] Bundles of cellulose microfibrils form macrofibrils and physically embed into different patterned scales to form mechanically strong networks, respectively.[16] Inspired by such unique structures, the aim of this paper is to design hybrid hydrogels containing hard colloidal cellulose nanofibrils (CNFs) connected by flexible polymer chains with improved mechanical properties as well as self-recovery behaviors.

To approach this purpose, we chose a noncovalent strategy due to its easy preparation and potential self-recovery of the materials. Our products consisted of three components: water, carboxylated CNFs, and tetra-arm poly(ethylene glycol) (PEG) having amine terminal groups (sample compositions in Table S1, Supporting Information). The CNF extracted from pulp paper by high-pressure homogenization and catalytic oxidation (2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO-mediated oxidation of primary alcohol groups to carboxylic acid groups), resulting in cellulose nanofibers with lateral diameter of 20−50 nm and length ranging from 400 to 600 nm (Figure S1, Supporting Information). The commercially available multiarm PEG used here had molecular weight of 5000 Da. On mixing with PEG in water, CNFs, which were highly entangled with each other, dispersed homogeneously owning to mutual negative-charged repulsion. As visualized using transmission electron microscopy (TEM) homogeneous dispersion is essential for increasing CNF effective surface area and bridging PEG. Indeed, one of the main motifs featured by natural materials is the colloidal reinforcement bound together by dynamic bonds on molecular level, allowing dissociation and reformation.[2,17] From the molecular structure depicted in Figure 1, it is envisioned that the concentrated CNF dispersion

Received: June 25, 2015
Accepted: July 16, 2015
Published: July 20, 2015

DOI: 10.1021/acsmacrolett.5b00422
ACS Macro Lett. 2015, 4, 829−833

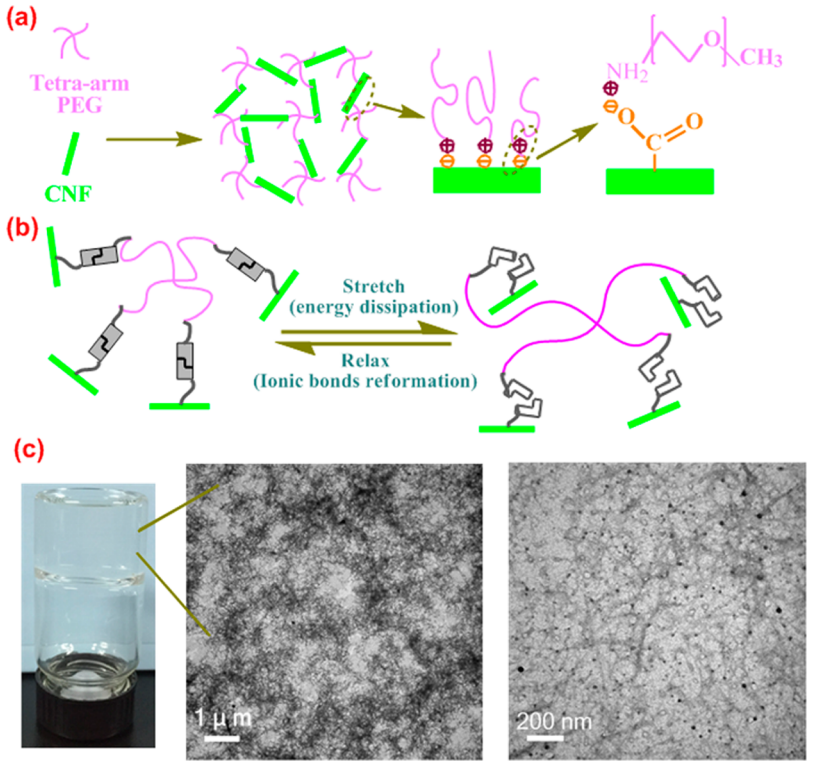


Figure 1. (a) Schematics and architecture for CNF-PEG hybrid networks where CNFs entangled with one another and dispersed uniformly by attractive interactions of negative-charged surface carboxylic groups with amine terminated PEG. (b) As the network is deformed, the PEG chains are stretched through the reversible ionic cross-links that act as sacrificial bonds and mechanical energy is dissipated. Once the stress is removed from the network, it can restore the original configuration. (c) The obtained transparent hydrogel (CNF loading of 1.5 wt %) and its TEM micrographs of the network. Note that the well-dispersed CNFs on different scales.

in an aqueous solution of PEG could form a high-strength supramolecular hybrid hydrogel due to its strong physical cross-linking stemming from the ionic bonded interactions between PEG and CNF. To verify our hypothesis, a series of samples with different concentrations of CNF dispersion (0.2−2 wt %) and a fixed PEG loading (2 wt %) were prepared. The results indicated that at 0.2 wt % CNF, the system was in the sol state, but gelation occurred when CNF concentration was raised to 0.5 wt %, as verified by the inverted vial method (Figure S2).

As described in Experimental Methods, the hydrogels can be obtained in a short time (10−15 min) by adding a dispersed aqueous suspension of CNFs (0.5−2 wt %, 5 mL) to a small proportion of PEG (2 wt %, 10 mL) in the absence of any chemical cross-links. TEM observation was applied to examine the dispersion of CNFs in PEG matrix, and the result indicated that nanofibrillar structure remained intact after the addition of PEG, suggesting the phase compatibility in the microscopic level. Besides, the polymer bridges are clearly noted between neighboring fibrils to form floc-like domains of the CNF network, leading to the reinforced supramolecular hybrids. It is hypothesized that by dynamic ionic-bridging between PEG and CNFs, efficient stress transfer would be attained.[17] In more detail, the storage moduli (G') and loss moduli (G'') were recorded for the colloidal networks with variable loading of CNF as a function of angular frequency at a fixed strain $\gamma = 1\%$ (Figure 2a). All these samples show a single plateau region in the dynamic moduli, and the G' values have a substantial elastic response and dominate over the G'' values in the whole range of frequencies. The mechanical reinforcement of the hybrids is facilely mediated by the loading of CNF, where the CNF 2 contained 2 wt % CNF gives a hydrogel the greatest G' value (934 Pa), inferring the reinforcement role of CNF (Figure 2b). This storage modulus from the CNF colloidal network at varying content is similar in comparison to previous reported model that described the rheological behaviors of CNF supramolecular hydrogels.[18]

As shown in Figure 2c, the strain sweep measurements indicated a broad linear regime up to $\gamma = 25.1\%$ for CNF 2. While with the applied strain was further increased, a significant decrease in G' and G'' was noted and a crossover occurred at the strain $\gamma = 63\%$. This deviation from original linearity to subsequent decrease in shear modulus is related to the collapse of the dynamical cross-linked structure and leads to a quasi-liquid state ($\tan \delta \approx 1.4-2.2$). Interestingly, we also note that the sample exhibits rapid recovery of its mechanical properties after a large amplitude oscillatory deformation, known as thixotropy (Figure 2d).[19] For example, when the strain returns a low value ($\gamma = 1\%$), the sample could recover its quasi-solid state ($\tan \delta \approx 0.2-0.6$) within 20 s (Figure S3). This result suggested that the reformation of ionic bridge between CNF and PEG was able to occur at room temperature under a low-shear condition. With increased loading of CNF, an improved recovery in G' was noted after the initial gel−sol transition and the time dependence of G' recovery was less pronounced than that of samples with a low CNF loading (strain sweep measurements of CNF 0.8 in Figure S4), inferring the rapid self-recovery of the hybrid was related to the bridge of dense regimes of CNF colloidal network.[20]

Besides the increase in G', the addition of CNF resulted in increased yield strain (determined from the oscillatory shear applied at the beginning of the decay of the G' in the strain-sweep profile) by more than an order of magnitude (Figure 3a).

DOI: 10.1021/acsmacrolett.5b00422
ACS Macro Lett. 2015, 4, 829−833

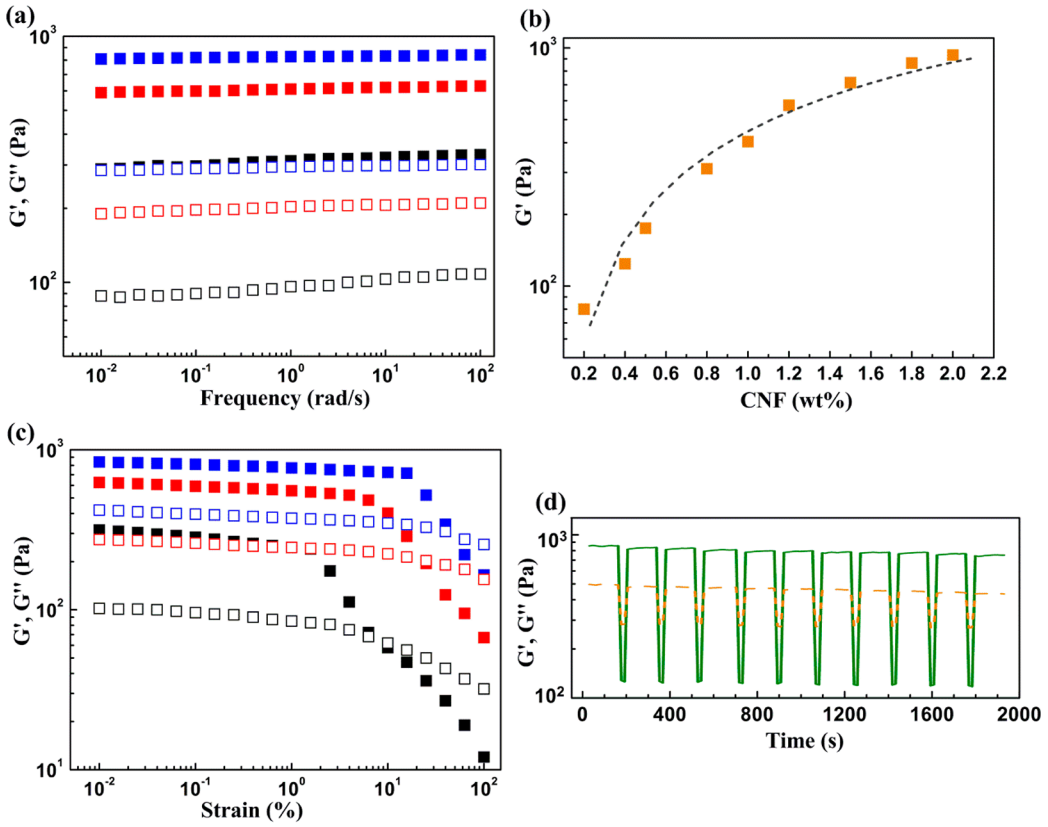


Figure 2. Rheological properties of hybrid hydrogels at 25 °C. (a) G' (solid) and G'' (open) values of CNF 0.8 (black), CNF 1.5 (red), and CNF 2 (blue) on frequency sweep from 0.01 to 100 rad/s. (b) Storage modulus as a function of CNF concentration determined in the linear regime (γ = 1%) at 6.283 rad/s. (c) G' (solid) and G'' (open) values on strain sweep for CNF 0.8 (black), CNF 1.5 (red), and CNF 2 (blue). (d) Period gel−sol reversible transition in continuous step-strain measurements for CNF 2 upon application of low strains 1% and high strains 80% for 120 and 60 s, respectively (G' solid lines, G'' dash lines).

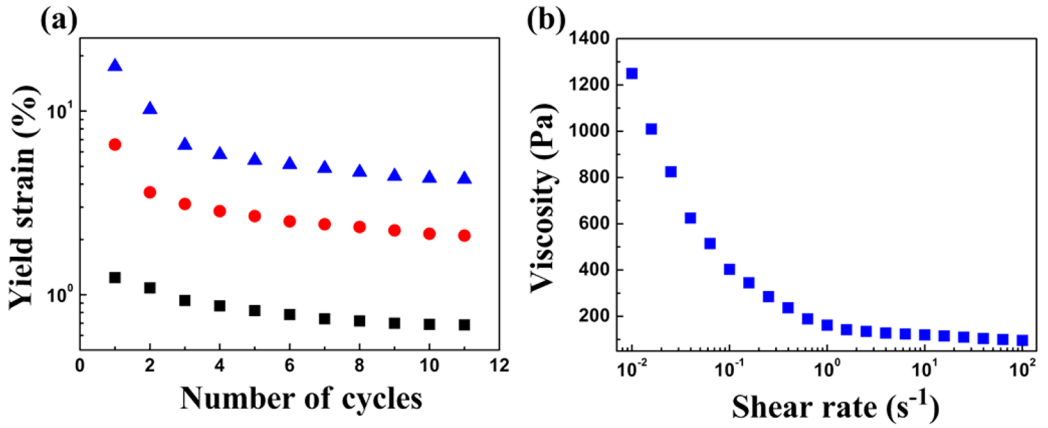


Figure 3. (a) Sequential yield strain for CNF 0.8 (black), CNF 1.5 (red), and CNF 2 (blue) hydrogels in repeated amplitude-sweep rheological tests. (b) Viscosity measurement on a CNF 2 hydrogels (γ = 1%).

This result may be stemmed from the reconfiguration of ionic bonds, allowing the colloidal networks to sustain the greater strain before the breakage of whole networks.[7] This observation suggests that the elastic modulus is depended on reversible ionic interactions between fibrils and PEG as well as entanglements between CNF.[21] Within the initial three cycles, there was a large decrease in yield strain, indicating the entanglement damage of strong, yet brittle CNF network. However, the decrease of yield strain was less pronounced in the subsequent cycles, inferring the cross-linked network was able to dissipate mechanical energy as well as to mediate self-recovery behavior within the strained condition. Furthermore, the viscosity test was performed on CNF 2 at 25 °C and 1% strain and a decrease in viscosity with increasing shear rate was noted (Figure 3b). This shear thinning phenomenon was related to the disruption of ionic interactions.[22] It has been proposed that the shear thinning behavior allows the mobility of broken domains to reconstruct with each other when stress is relaxed and plays a critical role in achieving self-recovery performance.[22]

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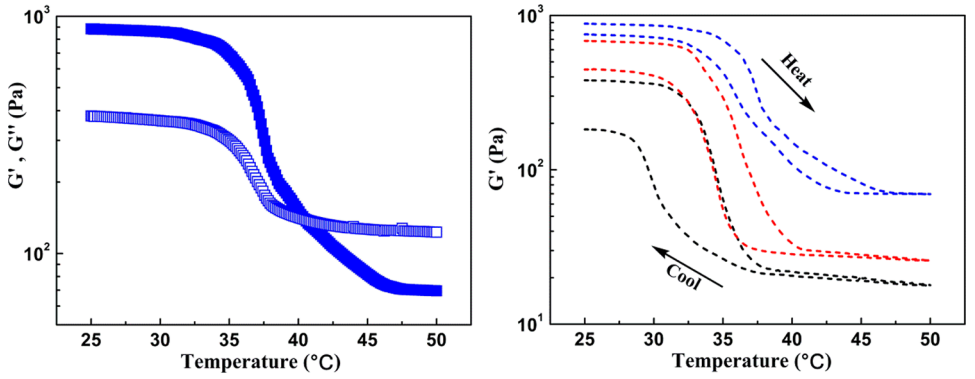

Figure 4. Thermo-sensitivity of the CNF hydrogels. (a) Temperature ramp test of G' (solid) and G'' (open) changes for CNF2 hydrogels. (b) Cyclic heating of the CNF 0.8 (black), CNF 1.5 (red), and CNF 2 (blue) hydrogels. The measurement was performed at an angular frequency of 6.28 rad/s and γ = 1% strain.

The recoverability of the thermal transition of the hybrid hydrogels was inspected by imposing heating−cooling cycles from 25 to 50 °C at a heating rate of 5 °C min^{-1} and back to 25 °C, where the values of G' and G'' were recorded at fixed frequency and strain values. One can note that both G' and G'' decreased rapidly as temperature was raised from 25 to 50 °C (Figure 4a). At a low temperature range (25−42 °C), G' was greater than G'', inferring a gel-like property. While with further heating process, G' decreased significantly faster than G'' and became much smaller than G'' at a higher temperature (>42 °C), signifying the transition from gelled state to sol state at a higher temperature. This dynamic transition suggests that the hybrids become weak at an elevated temperature due to the breakage of ionic bonding cross-links. Upon cooling, ionic bonds re- associated and formed the colloidal network when they were cooled. All the samples (0.8, 1.5, and 2 wt % CNF loadings) recovered their original G' and showed thermoreversible behavior (Figure 4b). The elastic modulus between the recovered and original gel was used to determine the recovery efficiency, and the results indicate that the CNF 1.5 and CNF 2 were able to attain 68 and 85%, respectively. With increased CNF content, the hysteresis loop became smaller, possibly due to increasing CNF loading leads to an increased number of cross-links within the PEG network. For example, adding 1.5 and 2 wt % CNF loading increased the G' to 447 and 753 Pa, respectively, suggesting efficient reinforcement of CNF in PEG polymer matrix up to 50 °C.

The obtained hybrid hydrogels prepared from >0.5 wt % CNF exhibited high mechanical properties and fast self-recovery capability where CNFs physically bridged by PEG in a transient network. The first feature may stem from the reinforcement of rigid CNFs, the main building unit of the 3D network. Nanofibril with strong hydrogen bonding in cellulose crystalline domains has been widely applied as reinforcement phase in composites due to its high elastic modulus (10^2 GPa) and tensile strength (~7 GPa). Since the colloidal network is simply built by bridging the flexible PEG to entangled CNF surface, the self-recovery process does not involve reassembly of polymer chains and is therefore fast. To stretch the bridged PEG chains, a force has to be applied to reduce entropy and increase enthalpy as flexible PEG chains are stretched after being released by the breakage of ionic cross-links.[10] The dynamic interactions acting as sacrificial bonds can be formed by ionic bridges between PEG multiple NH_3 arms and CNF surface carboxyl groups, leading to the hidden length being coiled up in a loop. As the chain is extended, the force on the polymer chains increases until the bond fracture of the sacrificial ionic bonds is reached.[11] Moreover, this stretching of chains against the entropy of the entire backbone is reversible and the ionic bonds can reform once the force is relaxed, indicating a self-recovery mechanism for energy dissipation without failure of the entire network.[10] Therefore, by combination of pseudocovalent bonding character and maintaining some degree of reversibility, we employ ionic cross-linking in conjunction with a rigid CNF skeleton network to mirror the soft + hard phase natural biomimetic strategy. Indeed, adsorbing flexible polymer chains, such as polyacrylamide, poly(*N*,*N*-dimethylacrylamide) and polypyrrolidone, to a nanocellulose surface via attractive interactions has been regarded to be an effective strategy to form dynamically cross-linked networks.[23,24] Therefore, the high CNF loading could lead to dense ionic bridge domains within a single polymer, allowing more built-in reversible sacrificial bonds to improve self-recovery properties.

In summary, we propose a facile and tunable fabrication process to create supramolecular hybrid hydrogels containing PEG bridged colloidal fibrillar CNFs with enhanced mechanical strength and self-recovery behavior. At room temperature, the CNF/PEG systems behave as elastic gels by increasing the CNF loading at 2 wt % PEG with $G' \sim \omega^0$ and $G' > G''$. Upon heating, the network undergoes a significant phase transition where ionic bridges lose part of their affinity to the surrounding CNFs and subsequently start a gel-to-sol change with largely decreased storage modulus. This was promoted by association and disassociation of reversible ionic cross-links in combination with the entanglement of fibrils to supramolecular networks. The present work would expand the potential applications of cellulose hydrogels in biomedical field (e.g., scaffolds for tissue engineering, vehicles for drug delivery) and pave a way toward combination of colloidal reinforcements with dynamic polymer of conformational freedom for supramolecular materials.

EXPERIMENTAL METHODS

The tetra-arm poly(ethylene glycol) (M_n = 5000 Da) was purchased from Alfa Aeser and all other reagent were analytical grade and used as received without further purification. The cellulose nanofibrils were attained from cotton pulp by high-pressure homogenization, then applied for TEMPO-mediated oxidation with a carboxylated content of 1.45 mmol/g. In a typical process of gelation, we added a dispersed suspension of CNFs in water (100 mg, 5 mL) to an aqueous solution of PEG (200 mg, 10 mL) at 25 °C. After 10 min stirring, the mixture became stiff, forming a transparent, self-standing elastomer. We

DOI: 10.1021/acsmacrolett.5b00422
ACS Macro Lett. 2015, 4, 829−833

prepared other samples similarly at different CNF loadings. The rheological properties of the hydrogels were measured using AR2000 rheometer (TA Instruments) with a 25 mm diameter parallel plate. The gap at the apex of the para-plate was set to be 1 mm and a thin layer of low viscosity silicon oil was applied to avoid water evaporation. To evaluate the self-recovery properties of the samples in response to applied stress strain, the following cyclic procedure was performed: γ = 1% for 120 s and γ = 80% for 60 s. The temperature dependency of the rheological properties of a hydrogel was performed from 25 to 50 °C at a rate of 5 °C min^{-1}. Transmission electron microscopy (TEM) observation was conducted using a JEM 1010 (JEOL) at 80 kV by procedures previously reported.[25]

■ ASSOCIATED CONTENT

Supporting Information

Experimental section detailing the isolation CNFs, compositions of the hydrogels, TEM images of CNF, images of hydrogels at different CNF loadings, strain sweep measurements for CNF 2, dynamic strain amplitude cyclic test for CNF 0.8, and rheological measurement for CNF aqueous suspension. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00422.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yangjun11@bjfu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by Fundamental Research Funds for the Central Universities (TD2011-10), National Natural Science Foundation of China (21404011, 31170557, 31470606), Research Fund for the Doctoral Program of Higher Education of China (20120014120006), National Science Fund for Distinguished Young Scholars (31225005), and Chinese Ministry of Education (113014A).

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DOI: 10.1021/acsmacrolett.5b00422
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