ACS Macro Letters

Letter

pubs.acs.org/macroletters

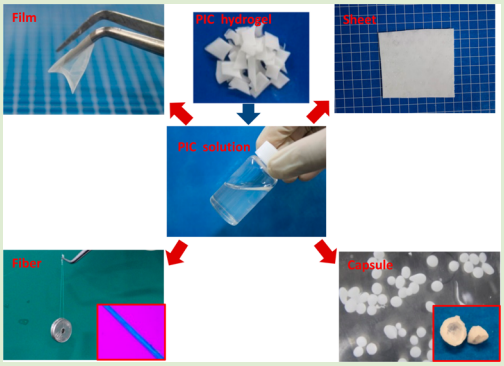
Free Reprocessability of Tough and Self-Healing Hydrogels Based on Polyion Complex

Feng Luo,[†,‡] Tao Lin Sun,[†] Tasuku Nakajima,[†] Takayuki Kurokawa,[†] Abu Bin Ihsan,[†] Xufeng Li,[§] Honglei Guo,[§] and Jian Ping Gong*[,†]

[†]Laboratory of Soft and Wet Matter, Faculty of Advanced Life Science, and [§]Laboratory of Soft and Wet Matter, Graduate School of Life Science, Hokkaido University, Sapporo 060-0810, Japan

Supporting Information

ABSTRACT: Tough hydrogels with facile processability to reform into various shapes are required in many practical applications. In this work, we reported that a novel, tough, and self-healing physical hydrogel based on polyion complex (PIC) can be dissolved in 4 M NaCl solution to form a PIC solution. The PIC solution can be easily reprocessed into various shapes, such as thin films, sheets, fibers, and capsules, by using simple methods, such as casting and injection, while maintaining excellent mechanical properties comparable to, or even better than, the original hydrogel. The reprocessability and robust mechanical properties of PIC hydrogels are promising for practical applications in soft materials, especially in 3D/4D printing technology.



Hydrogels are fascinating materials with high potential for applications in smart structures and biomedical engineering.[1−6] Any given application requires a specific combination of mechanical properties including toughness, stiffness, damping, fatigue resistance, and self-healing. In addition, a facile processing ability is also very important for industrial manufacturing. Developing tough and self-healing hydrogel materials that can be easily processed into various shapes is important for "real world" applications. In our previous work, we developed tough double network hydrogels based on a sacrificial bond mechanism.[7−9] When the sacrificial bonds are composed of reversible bonds, including hydrogen bonds,[10,11] hydrophobic interactions,[12] $\pi-\pi$ stacking,[13] or ionic bonds,[14,15] self-healing properties can be incorporated in hydrogels, in addition to increasing toughness. Studies along these lines have successfully produced tough double network hydrogels with self-healing properties.[3,16−18]

Tough hydrogels with tailor-made shapes are required for many practical applications. For example, injectable tough hydrogels are required for cartilage substitutes,[19,20] tough hydrogel microcapsules are required for drug carriage and release,[21,22] and tough hydrogel fibers are required as surgery thread. Furthermore, controlled curvature and transparency are necessary requirements to use tough hydrogels as contact lens, etc.[23] For these diverse applications, hydrogels that are both mechanically robust and easily processable are required. In principle, physical hydrogels can be easily processed into desired shapes. However, common hydrogels are mechanically weak. Robust hydrogels with facile processability are rarely reported. Recently, we have developed a class of novel tough and self-healing hydrogels from oppositely charged polymers.[24] The oppositely charged polyelectrolytes form polyion complexes (PIC) of a wide strength distribution, which results in dynamic cross-linking of an extremely wide scale of bond lifetimes. The strong, long lifetime bonds serve as permanent cross-linking, imparting elasticity, whereas the weak, short lifetime bonds function as reversible cross-linking that break and reform during deformation to dissipate energy. By this mechanism, the weak bonds serve as reversible sacrificial bonds and give the hydrogels high toughness, self-healing, and adhesive properties.

In this work, we report that the reversible ionic bonds of PIC hydrogels also allow for dramatic reprocessability of the material. The PIC solution, obtained by dissolving PIC hydrogel in concentrated NaCl solution, can be freely reprocessed into various shapes of hydrogels such as thin films, sheets, fibers, and capsules by dialysis in water at ambient temperature. The reprocessed samples also possess high toughness comparable or even higher than the mother PIC hydrogel.

The mechanism of the reprocessability is illustrated in Figure 1. On the base of the ionic shielding effect, all of the ionic bonds in the PIC physical hydrogel can be disassociated in high NaCl solution. Thus, the PIC hydrogel forms a uniform solution when it is immersed in high NaCl solution. Reversely, when the PIC solution is dialyzed in water, the small co-ions and counterions of the polyelectrolytes are removed from the system and, as a result, the ions associate into polyion

Received: July 21, 2015
Accepted: August 20, 2015
Published: August 21, 2015

DOI: 10.1021/acsmacrolett.5b00501
ACS Macro Lett. 2015, 4, 961−964

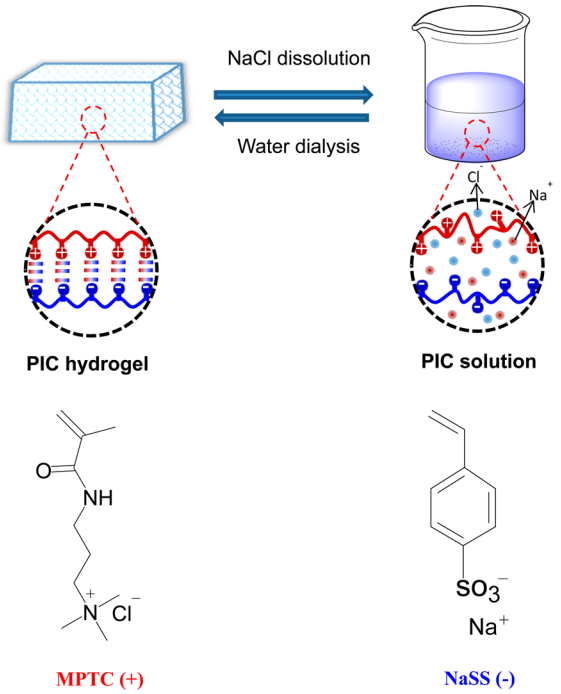


Figure 1. Schematic illustration for the reprocessing of polyion complex (PIC) hydrogels and the structure of monomers used in this work.

complexes to form tough physical hydrogels again. Taking advantage of this reversible sol−gel transformation mechanism, one can reform the tough and self-healing hydrogels into desired shapes easily.

To demonstrate this fact, we show a typical example of PIC hydrogel, sequentially polymerized from 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC) as the first monomer and sodium *p*-styrenesulfonate (NaSS) as the second monomer in the same conditions as in our recent report (see Supporting Information).[24] The PIC hydrogel, named PMPTC/PNaSS (M_w of PMPTC ~ 4.6×10^6 g/mol, and M_w of PNaSS ~ 7.7×10^5 g/mol), was immersed in water to reach the equilibrium state. During this process, the gel shrank by the dialysis of small counterions and formation of multiple ion bonds. PIC hydrogel became very tough and exhibited self-healing ability after dialysis. It is stable in low salt concentration but dissolves in concentrated saline solution (>3 M).[24] The equilibrated hydrogel was cut into small pieces and then immersed in 4 M NaCl aqueous solution at 60 °C for fast disassociation. As shown in Figure 2, with increasing immersing time, the white PIC gel gradually swells and becomes transparent. After 5 h, the hydrogel was completely dissolved in the NaCl solution to form a translucent solution. The viscosity of solution was tuned by polymer concentration to facilitate further processing.

Using the simple methods shown in Figure 3a and Movies 1 and 2, the solution was reformed easily into various shapes. Figure 3b−e shows thin films, sheets, fibers, and capsules reformed by curtain coating, mold-dialysis, injecting spinning, and dropping-dialysis, respectively. All of this flexibility in processing can be explained by the schematic illustration shown in Figure 1. That is, when the polyelectrolyte solution contacts with water, the small co-ions and counterions in solution diffuse into water due to the difference in concentration. The oppositely charged polyelectrolytes form multiple ionic bonds to reform the PIC hydrogel. Particularly, for injecting spinning, the fast flow of deionized water elongates the polymer chains and results in the formation of PIC fibers that exhibit strong orientation. For dropping-dialysis, the counterions in the outer surface of the polyelectrolyte drop first exchange with water and form a hydrogel layer that plays a role as a template to induce the reconstruction of the inner solution.

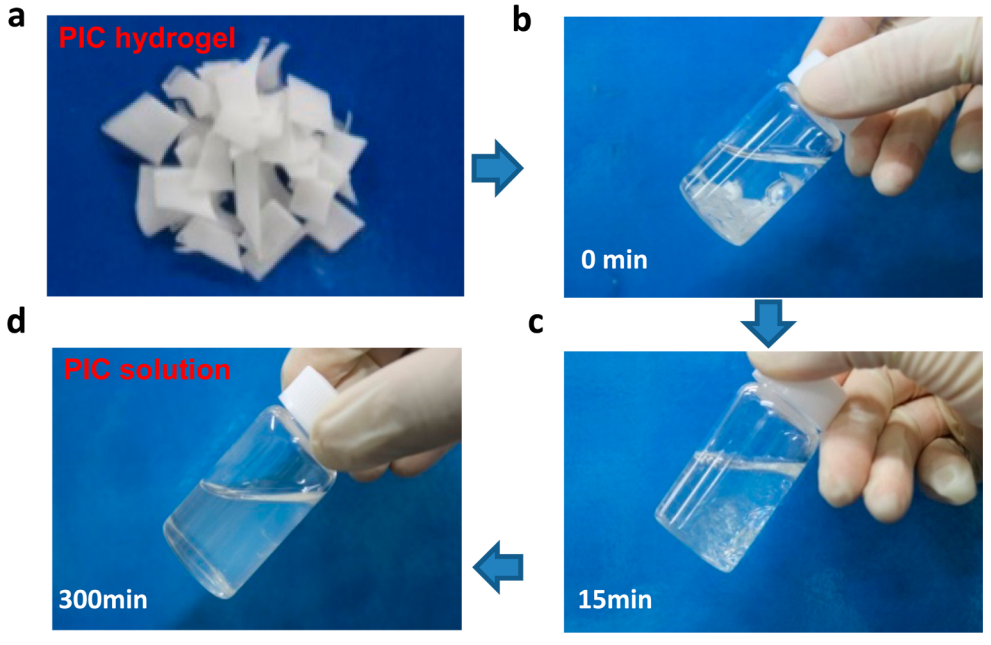


Figure 2. Pictures demonstrating the disassociation of the PIC hydrogel PMPTC/PNaSS in 4 M NaCl solution. (a) The original PIC hydrogel that was cut into small pieces; (b) Initial deposition of the PIC hydrogel in 4 M NaCl solution; (c) After 15 min, the sample became transparent due to ionic bond disassociation; (d) The PIC hydrogel was completely dissolved in 4 M NaCl after 300 min to give a uniform (translucent) solution with a polymer concentration of 80 g/L.

DOI: 10.1021/acsmacrolett.5b00501
ACS Macro Lett. 2015, 4, 961−964

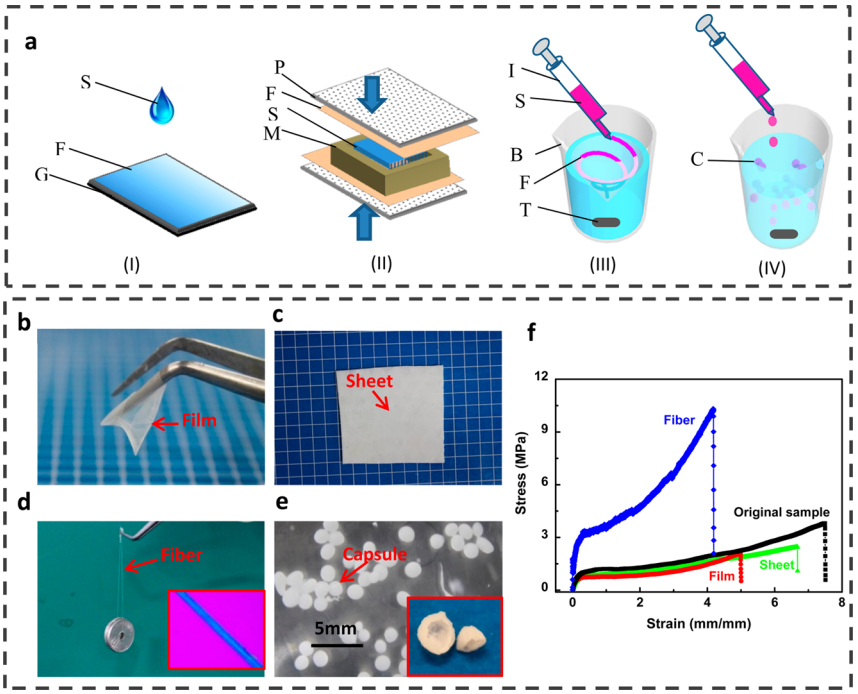


Figure 3. Pictures demonstrating the reformability of PIC hydrogel PMPTC/PNaSS into film, fiber, and capsule. (a) Schematics of curtain coating (I), mold-dialysis (II), injecting spinning (III), and dropping-dialysis (IV) to reform the PIC hydrogel. In (I): S, PIC solution; F, PIC thin film; G, glass sheet. In (II): P, multihole plastic sheets; F, selectively permeable membranes; S, PIC solution; M, silicone rubber spacer. The mold was sealed by pressing force along the arrow direction. In (III) and (IV): I, syringe; S, PIC solution; B, beaker; F, PIC fiber; T, magnetic stirrer; C, PIC capsule. (b) Image of reformed PIC thin film (thickness: 0.03 mm). (c) Image of reformed PIC sheet. (d) Image of reformed PIC fiber (diameter: 0.1 mm), which can load the weight of two coins (~8 g); inset picture shows the orientation of a fiber observed by a polarized microscope with red filter (λ-plate) at −45° to the fiber axis direction. (e) Image of a reformed PIC capsule; inset picture shows the hollow structure of the capsule that was cut into two hemispheres. (f) Stress−strain curves of the reformed PIC thin film, sheet, and fiber, in comparison with original sample.

The film reformed by curtain coating can be as thin as 30 μm with good flexibility and toughness (Figure 3b). The sheet reformed by mold-dialysis shows similar appearance as the original hydrogel (Figure 3c). Also, the reformed fiber (diameter ~ 100 μm) with obvious orientation, as confirmed by the birefringence in the inset picture of Figure 3d, is quite strong and flexible. In addition, the hydrogel capsules with hollow structure and tunable wall thickness are formed after water dialysis (Figure 3e). Furthermore, we also confirmed that some functional microparticles can be well dispersed in this PIC solution. Such complex solution also can be freely reprocessed and can result in special properties. For example, magnetic hydrogel capsules are obtained from the PIC solution mixed with Fe_3O_4 microparticles, as shown in Movie 3. Meanwhile, the reformed samples show excellent mechanical properties, as shown in Figure 3f. The strength and toughness of the reformed film and sheet are almost comparable to that of original hydrogel. For example, the Young's modulus E of the reformed film, sheet, and original hydrogels are 7.9, 6.3, and 8.4 MPa, respectively. Meanwhile, the fracture stress σ_f of the reformed film, sheet, and original hydrogels are 2.1, 2.4, and 3.6 MPa, respectively. Surprisingly, the reformed fiber with good orientation shows much improved properties in modulus (24.2 MPa), fracture stress (10 MPa), and work of extension (23 MJ/m^3) than those of the original hydrogel. Although many polymer systems can be reformed via sol−gel transition upon temperature change or by gelation via multivalence ions, to our knowledge, no previously published literature reported a successful ability to reform tough hydrogels.

Although the reprocessing behavior of the PIC system is based on reversible ionic bonds, the homogeneously entangled structure of polymer chains in the dissolved solution should also be required for the formation of tough gel. To justify this argument, we also reformed two other hydrogels based on ionic bond formation. One is polyampholyte (PA) gel of P(MPTC-*co*-NaSS) synthesized from equal molar copolymerization from MPTC and NaSS (see Supporting Information),[17] and the other is a PIC gel of PMPTC/PNaSS-b formed directly by equal molar blending of PMPTC (M_w ~ 4.6 × 10^6 g/mol) and PNaSS (M_w ~ 7.7 × 10^5 g/mol) that were separately polymerized (see Supporting Information). As reported in our previous paper, the virgin P(MPTC-*co*-NaSS) gel is very tough, comparable to the PMPTC/PNaSS gel. However, as shown in Figure 4, the reformed PA gel P(MPTC-*co*-NaSS) is very weak, with E and σ_f of 0.1 and 0.07 MPa, respectively. Furthermore, the directly blended sample of PMPTC/PNaSS-b with E of 1.6 MPa and σ_f of 0.97 MPa is also much weaker than that of the sample PMPTC/PNaSS (E of 6.3 MPa and σ_f of 2.4 MPa) reformed from a PIC hydrogel solution formed by sequential polymerization. As reported in our previous work,[17] the PA hydrogel is cross-linked by ionic bonds to form both intra- and interchain interactions. Once this structure is completely disassociated by saline solution, the relatively diluted polymer concentration favors the intrachain ion bond formation, which in turn suppresses the polymer entanglement and interchain bonding. In contrast, the PIC solution only forms interchain ionic bonding. Therefore, even at relatively dilute concentration, polymers are in an extended conformation that favors the occurrence of polymer entanglement and ion

DOI: 10.1021/acsmacrolett.5b00501
ACS Macro Lett. 2015, 4, 961−964

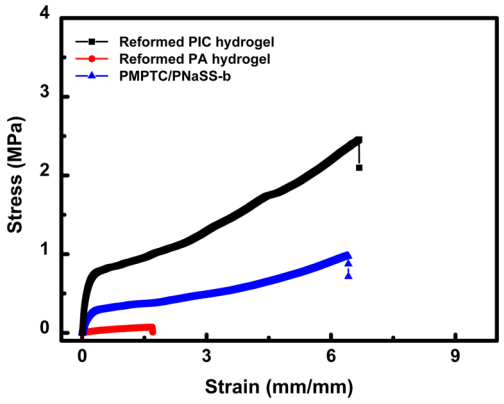


Figure 4. Comparison of stress−strain curves of three different hydrogels with ionic bonds. PIC hydrogel denotes the sample reformed from PIC hydrogel PMPTC/PNaSS synthesized by sequential polymerization, PA hydrogel denotes the sample reformed from polyampholyte (PA) hydrogel P(MPTC-*co*-NaSS), and PMPTC/PNaSS-b denotes the sample formed by blending PMPTC and PNaSS directly. The polymer concentrations in the reformed solutions for PIC hydrogel, PA hydrogel, and blend were 80, 80, and 150 g/L, respectively. The water content of the three reformed samples was 53 ± 5, 58 ± 7, and 54 ± 6%, respectively.

complex formation during reconstruction. On the other hand, the direct blending of oppositely charged PMPTC and PNaSS leads to inhomogeneous precipitation, where strong polyion complexes are formed at the interface of the two solutions, which quenches further reaction. Thus, the PIC hydrogel solution formed by sequential polymerization assures the uniform dispersion of polymer chains and as a result, the reformed PIC hydrogels have excellent mechanical properties.

In summary, the tough and self-healing PIC hydrogel formed by sequential polymerization can be reformed into various shapes at room temperature by a simple method. The reformed hydrogels show excellent mechanical properties comparable to the original PIC gel. The tailor-made properties of this PIC hydrogel would significantly promote the practical application of such hydrogels, especially by combining with 3D/4D printing technology in additive manufacturing to print custom designed hydrogel structures.

■ ASSOCIATED CONTENT

Supporting Information

Materials, measurements, synthesized procedures, reforming methods, and reprocessing movies. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00501.

(PDF)
(AVI)
(AVI)
(AVI)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gong@mail.sci.hokudai.ac.jp.

Present Address

‡College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China (F.L.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was funded by ImPACT Program of Council for Science, Technology and Innovation (Cabinet Office, Government of Japan) and the Grant-in-Aid for JSPS Fellows relating to JSPS Postdoctoral Fellowships for Foreign Researchers (No. P12340) from JSPS. We also thank Dr. Daniel R. King for checking and editing grammar.

■ REFERENCES

(1) Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R. *Adv. Mater.* **2006**, *18* (11), 1345−1360.
(2) Calvert, P. *Adv. Mater.* **2009**, *21* (7), 743−756.
(3) Sun, J. Y.; Zhao, X. H.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. G. *Nature* **2012**, *489* (7414), 133−136.
(4) Zhao, X. *Soft Matter* **2014**, *10* (5), 672−687.
(5) Henderson, K. J.; Shull, K. R. *Macromolecules* **2012**, *45* (3), 1631−1635.
(6) Li, J.; Illeperuma, W. R.; Suo, Z.; Vlassak, J. J. *ACS Macro Lett.* **2014**, *3*, 520−523.
(7) Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. *Adv. Mater.* **2003**, *15* (14), 1155−1158.
(8) Nakajima, T.; Kurokawa, T.; Furukawa, H.; Yu, Q. M.; Tanaka, Y.; Osada, Y.; Gong, J. P. *Chin. J. Polym. Sci.* **2009**, *27* (1), 1−9.
(9) Gong, J. P. *Soft Matter* **2010**, *6* (12), 2583−2590.
(10) Gao, H.; Wang, N.; Hu, X.; Nan, W.; Han, Y.; Liu, W. *Macromol. Rapid Commun.* **2013**, *34* (1), 63−68.
(11) Cordier, P.; Tournilhac, F.; Soulié-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451* (7181), 977−980.
(12) Hao, J.; Weiss, R. *Macromolecules* **2011**, *44* (23), 9390−9398.
(13) Burattini, S.; Colquhoun, H. M.; Fox, J. D.; Friedmann, D.; Greenland, B. W.; Harris, P. J.; Hayes, W.; Mackay, M. E.; Rowan, S. J. *Chem. Commun.* **2009**, *44*, 6717−6719.
(14) Henderson, K. J.; Zhou, T. C.; Otim, K. J.; Shull, K. R. *Macromolecules* **2010**, *43* (14), 6193−6201.
(15) Hunt, J. N.; Feldman, K. E.; Lynd, N. A.; Deek, J.; Campos, L. M.; Spruell, J. M.; Hernandez, B. M.; Kramer, E. J.; Hawker, C. J. *Adv. Mater.* **2011**, *23* (20), 2327−2331.
(16) Haque, M. A.; Kurokawa, T.; Kamita, G.; Gong, J. P. *Macromolecules* **2011**, *44* (22), 8916−8924.
(17) Luo, F.; Sun, T. L.; Nakajima, T.; Kurokawa, T.; Zhao, Y.; Ihsan, A. B.; Guo, H. L.; Li, X. F.; Gong, J. P. *Macromolecules* **2014**, *47*, 6037−6046.
(18) Sun, T. L.; Kurokawa, T.; Kuroda, S.; Ihsan, A. B.; Akasaki, T.; Sato, K.; Haque, M. A.; Nakajima, T.; Gong, J. P. *Nat. Mater.* **2013**, *12* (10), 932−937.
(19) Macaya, D.; Spector, M. *Biomed. Mater.* **2012**, *7* (1), 012001.
(20) Johnson, T. D.; Christman, K. L. *Expert Opin. Drug Delivery* **2013**, *10* (1), 59−72.
(21) Tokarev, I.; Minko, S. *Adv. Mater.* **2010**, *22* (31), 3446−3462.
(22) Qiu, Y.; Park, K. *Adv. Drug Delivery Rev.* **2012**, *64*, 49−60.
(23) Nicolson, P. C.; Vogt, J. *Biomaterials* **2001**, *22* (24), 3273−3283.
(24) Luo, F.; Sun, T. L.; Nakajima, T.; Kurokawa, T.; Zhao, Y.; Sato, K.; Ihsan, A. B.; Li, X.; Guo, H.; Gong, J. P. *Adv. Mater.* **2015**, *27* (17), 2722−2727.

DOI: 10.1021/acsmacrolett.5b00501
ACS Macro Lett. 2015, 4, 961−964