Supporting Information

for

Metal-Coordination Complexes Mediated Physical Hydrogels with High Toughness, Stick-Slip Tearing Behavior, and Good Processability

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Table S1. Recipes of precursor solutions for the synthesis of copolymers with different compositions.

f	Concentration (wt%)		
	AAm	AAc	KPS
8%	18.4	1.6	0.2
10%	18.0	2.0	0.2
15%	17.0	3.0	0.2
20%	16.0	4.0	0.2
25%	15.0	5.0	0.2

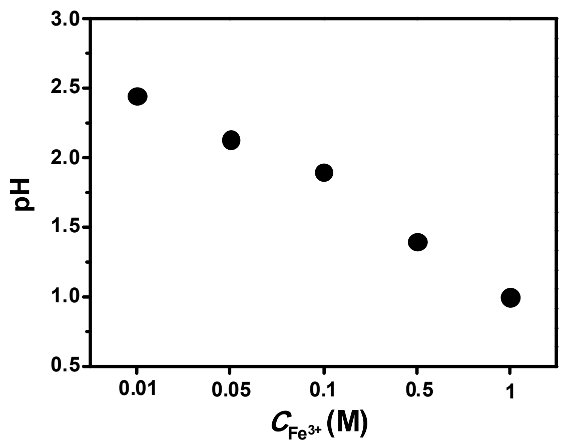

Figure S1. pH values of $FeCl_3$ aqueous solutions with different concentrations.

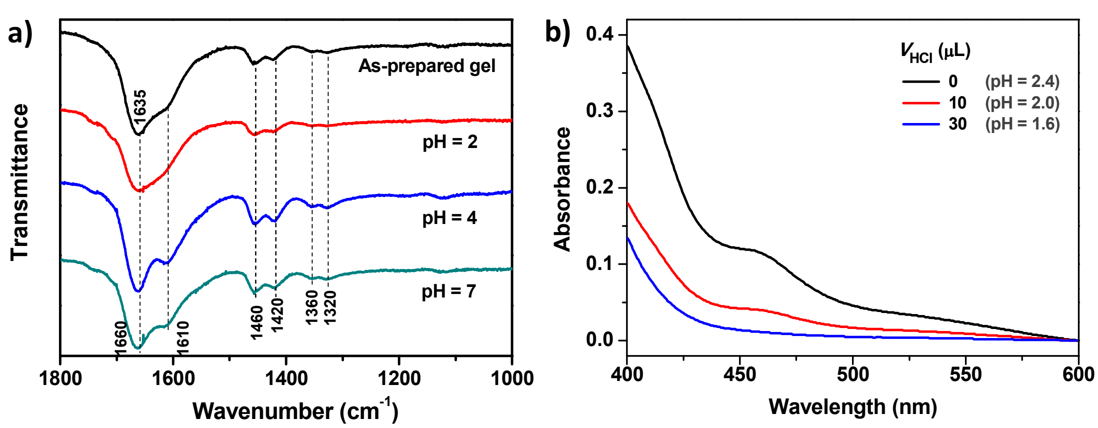

Figure S2. (a) FTIR spectra of the as-prepared P(AAm-*co*-AAc) gel (*f* = 10%) and that after being swelled in solutions with different pH. (b) UV-vis spectra of the mixture of 3 mL of 2 mg/mL P(AAm-*co*-AAc) (*f* = 10%) and 40 μL of 0.1 M $FeCl_3$ solution with addition of a certain amount of 6 M HCl solution. The pH values of the system after addition of HCl solution are noted in (b).

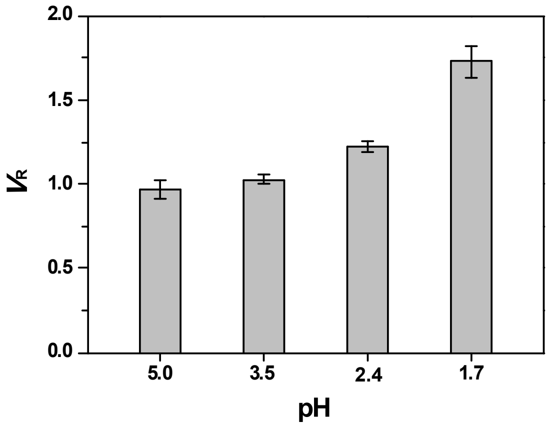

Figure S3. Volume ratio of the equilibrated gel (f = 15%) swelled in solutions with different pH to that swelled in pure water. The samples with a disc shape were cut from a bulk equilibrated gel and swelled in acidic solutions for 24 h to achieve the equilibrium state. The volume ratio V_R was calculated as $V_R = (d/d_0)^3$, in which d and d_0 are the diameter of gels before and after swelling in acidic solutions. Error bars represent standard deviation of the mean.

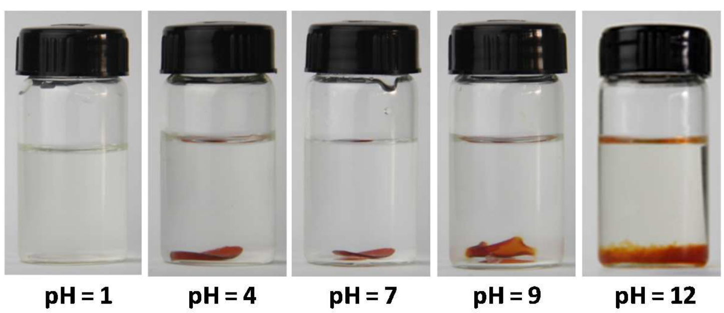

Figure S4. Photos of the equilibrated gels (f = 20%) incubated in solutions with different pH for 48 h. The pH of solutions was adjusted by addition of HCl or NaOH.

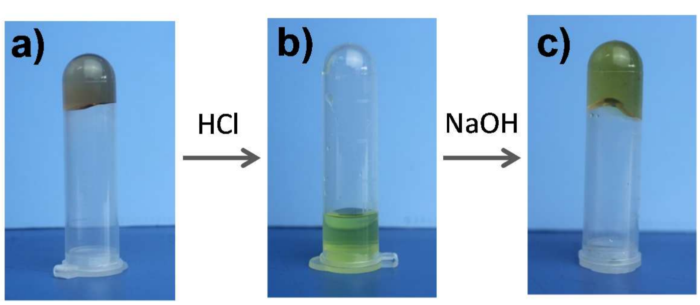

Figure S5. Reversible sol-gel transition mediated by pH. 10 μL of 1 M $FeCl_3$ solution was added to 1 mL of 5 wt% P(AAm-*co*-AAc) solution (f = 8%), resulting in the sol-to-gel transition of the sample (a). Then, 50 μL of 3 M HCl solution was added to the preformed gel, leading to gel-to-sol transition (b). The solution was regelled by gradually adding 40 μL of 3 M NaOH solution (c).

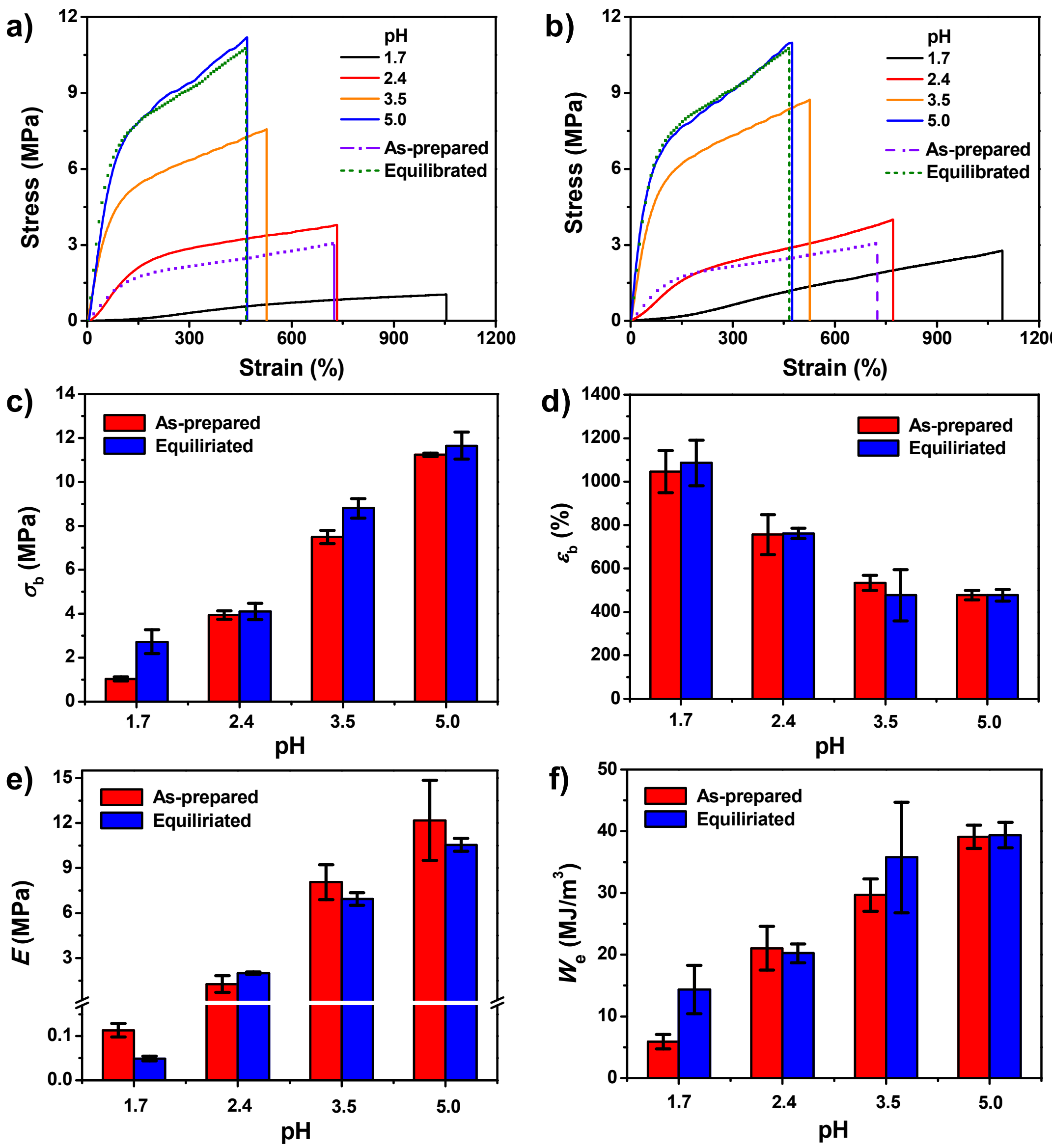

Figure S6. Mechanical properties of P(AAm-*co*-AAc) hydrogels with f = 15% incubated in solutions with different pH. Tensile stress-strain curves (a,b) and corresponding breaking stress σ_b (c), breaking strain ε_b (d), tensile modulus E (e), and extension work W_e (f) of the gels. The tested samples were the as-prepared (a) and equilibrated (b) gels after being swelled in solutions with different pH. The tensile curves of original as-prepared and equilibrated gels were also presented in (a) and (b) for comparison. Error bars represent standard deviation of the mean.

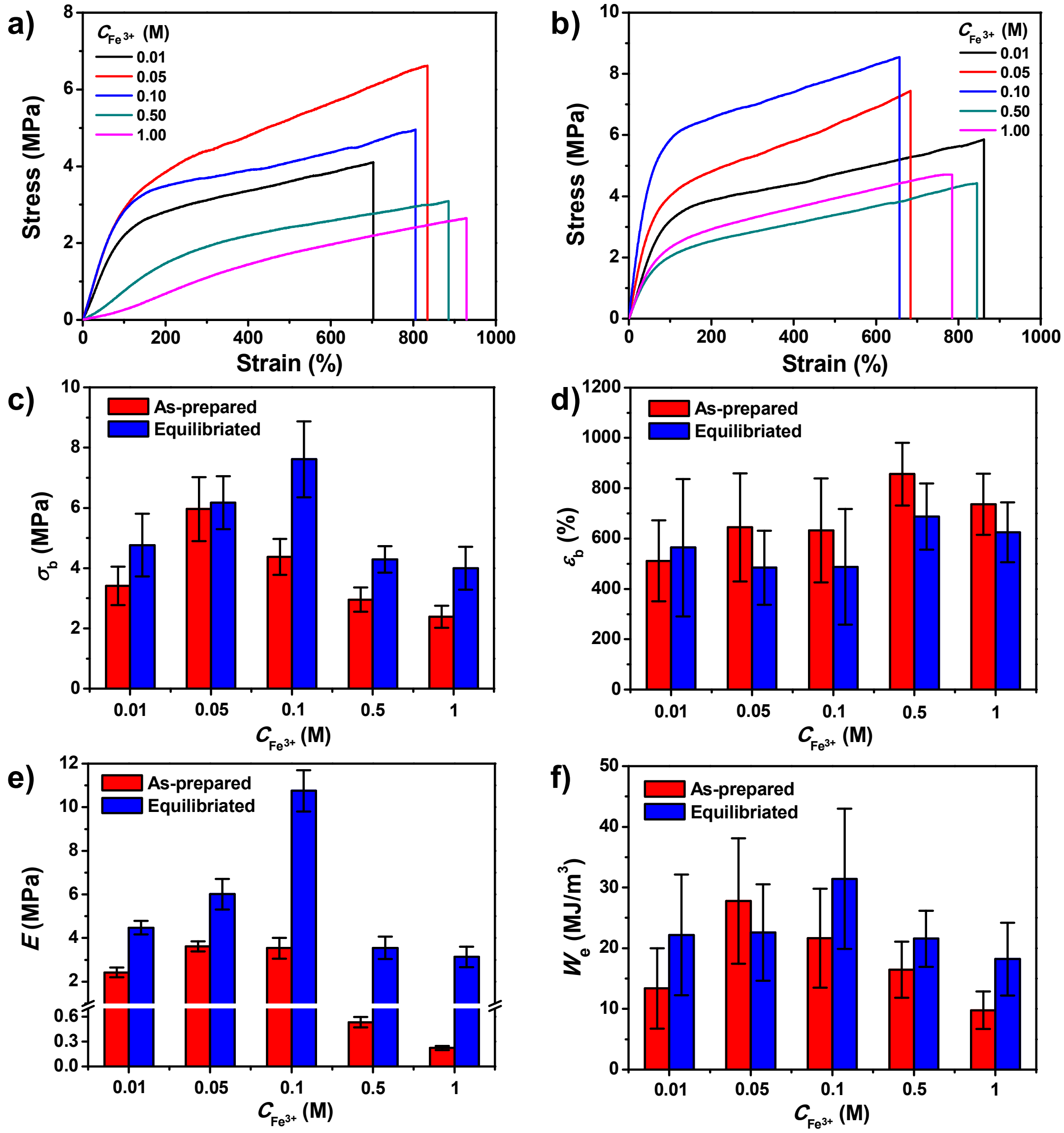

Figure S7. Mechanical properties of as-prepared and equilibrated P(AAm-*co*-AAc) gels (f = 15%) prepared by soaking the cast films in $FeCl_3$ solutions with different concentrations C_{Fe3+} and then reswelling them in water. Tensile stress-strain curves of the as-prepared (a) and equilibrated (b) gels and the corresponding breaking stress σ_b (c), breaking strain ε_b (d), tensile modulus E (e), and extension work W_e (f). Error bars represent standard deviation of the mean.

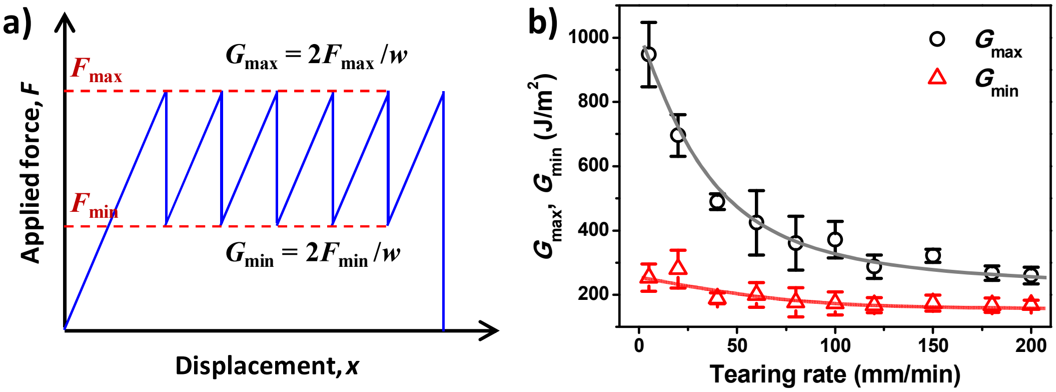

Figure S8. (a) Typical F(x) curve of stick-slip tearing. G_{max} and G_{min}, corresponding to the maximum force F_{max} and minimum force F_{min}, respectively, were calculated as $G_{max} = 2F_{max}/w$ and $G_{min} = 2F_{min}/w$. (b) Rate dependent G_{max} and G_{min} of equilibrated P(AAm-*co*-AAc) gel (f = 10%). The corresponding F(x) curves are shown in Figure 5d. Error bars represent standard deviation of the mean.

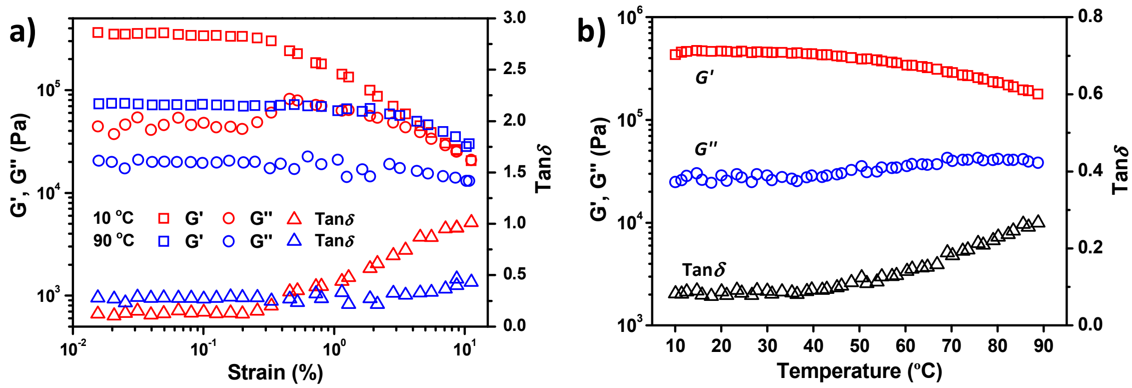

Figure S9. (a) Strain-sweeps of equilibrated P(AAm-*co*-AAc) gel (f = 15%) at 10 and 90 °C. The frequency was kept as 1 rad/s. (b) Temperature-sweep of equilibrated P(AAm-*co*-AAc) gel (f = 15%) at frequency of 1 rad/s and strain amplitude of 0.05%.

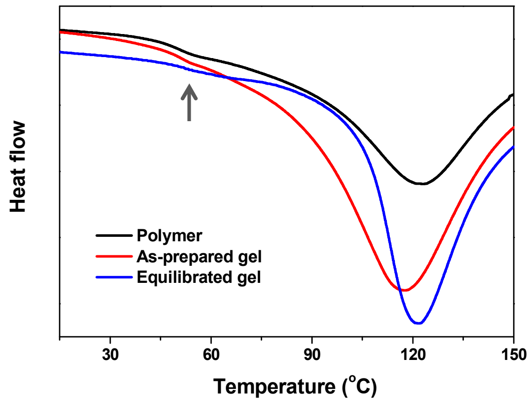

Figure S10. Thermographs of the as-prepared and equilibrated P(AAm-*co*-AAc) physical gels with coordinate complexes, as well as the P(AAm-*co*-AAc) solution without coordinate complexes (f = 25%). Heating rate: 10 °C/min. The peaks at ~50 °C (indicated by the arrow) and ~110 °C correspond the destruction of hydrogen bonds and the boiling point of water, respectively.

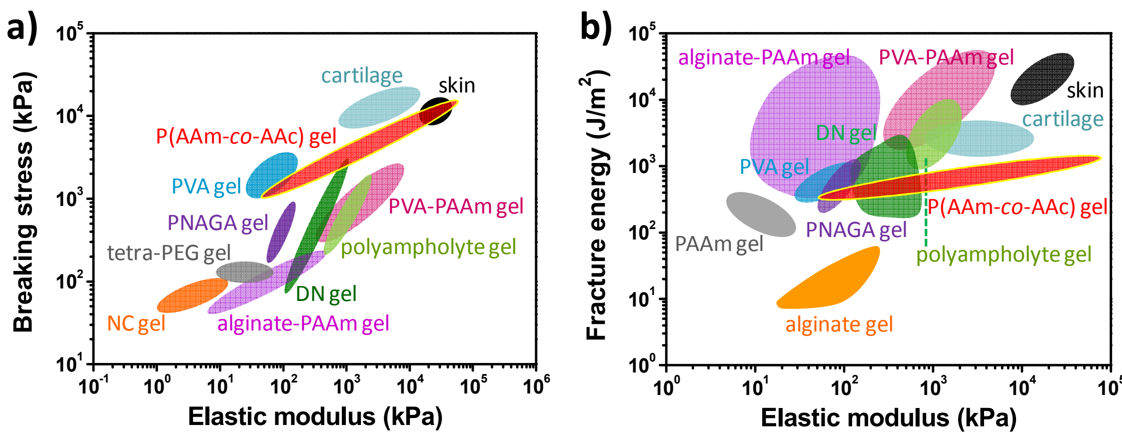

Figure S11. Material property charts for various soft materials. (a) Tensile breaking stress versus elastic modulus. (b) Tearing fracture energy versus elastic modulus. Materials include the P(AAm-*co*-AAc) gels in this work, poly(vinyl alcohol) (PVA) gel,[S1] double network (DN) gel,[2] nanocomposite (NC) gel,[6] alginate-polyacrylamide (alginate-PAAm) gel,[23] PVA-PAAm gel,[40] poly(sodium *p*-styrenesulphonate-*co*-3-methacryloylaminopropyl-trimethylammonium) polyampholyte gel,[11] PAAm gel,[23] tetra-arm polyethylene glycol (tetra-PEG) gel,[7] poly(*N*-acryloyl glycinamide) (PNAGA) gel,[15] alginate gel,[23] as well as cartilage and skin.[S2,S3] Among the synthetic gels, the PVA gel, PNAGA gel, alginate gel, and P(AAm-*co*-AAc) gel are physical hydrogels. Only several tough gels with permanent networks are selected for comparison with physical and biological gels.

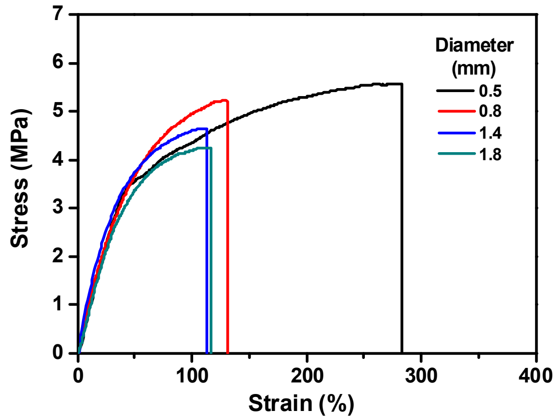

Figure S12. Tensile stress-strain curves of equilibrated P(AAm-*co*-AAc) gel fibers (*f* = 15%) with different diameters. Stretch rate: 100 mm/min. Super-glue was used to fix the sample on the tensile gripper so that to avoid slippage. The breaking of samples always occurs at the adhesion site, resulting in smaller breaking strain than that of gel film measured by using dumbbell-shaped sample.

Movie S1. Stick-slip instability during the tearing test of equilibrated P(AAm-*co*-AAc) gel (*f* = 10%) at stretch rate (the pulling velocity of the cross-head) of 100 mm/min.

Movie S2. Shape retention of the robust equilibrated gel (*f* = 15%) with a helical structure.

References

(S1) Zhang, L.; Zhao, J.; Zhu, J. T.; He, C. C.; Wang, H. L. Anisotropic tough poly(vinyl alcohol) hydrogels. *Soft Matter* **2012**, *8*, 10439–10447.

(S2) Nakayama, A.; Kakugo, A.; Gong, J. P.; Osada, Y.; Takai, M.; Erata, T.; Kawano, S. High mechanical strength double-network hydrogel with bacterial cellulose. *Adv. Funct. Mater.* **2004**, *14*, 1124–1128.

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