Supplementary Information

Synergistic effect of quaternary ammonium hydroxide and crown ether on the rapid and clear dissolution of cellulose at room temperature

Tadashi Ema,*^a Takuzo Komiyama,^b Satomi Sunami^a and Takashi Sakai*^a

^a Division of Chemistry and Biotechnology, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan.

^b Japan Exlan Co., Ltd., Kanaoka-higashimachi, Okayama 704-8510, Japan.

[A] The dissolution of cellulose in various quaternary onium hydroxidesS	31
[B] Control experiments for the cellulose dissolutionS	3

[A] The dissolution of cellulose in various quaternary onium hydroxides.

We investigated the effects of KBr and 18C6 using the following quaternary onium hydroxides: tetramethylammonium hydroxide (TMAH), benzyltrimethylammonium hydroxide (BTMAH), tetraethylammonium hydroxide (TEAH), and tetrabutylphosphonium hydroxide (TBPH). A mixture of cellulose (200 mg for TBPH and 20 mg for TMAH, BTMA, and TEAH), KBr (100 mM), and/or 18C6 (2.0 M for TBPH and 1.0 M for TMAH, BTMA, and TEAH) in 40% quaternary onium hydroxide (2 mL) was stirred at room temperature for 24 h. The results are shown in Fig. S1. We observed that 200 mg of cellulose could not be dissolved in 2 mL of 40% TMAH, BTMAH, or TEAH and that any attempt to improve the conditions was unsuccessful. 20 mg of cellulose was dissolved in 40% BTMAH or TEAH after stirring at room temperature for 24 h and then mild heating, while the solubility of cellulose in 40% TMAH could not be improved by decreasing the amount of cellulose or heating, and the addition of 18C6 formed a gel precipitate. On the other hand, TBPH had a good dissolution power like TBAH, and the effects of KBr and 18C6 that are similar to those observed for TBAH were observed. A trend can be seen that increasing the bulkiness of the substituent of quaternary onium cation increased the dissolution power.

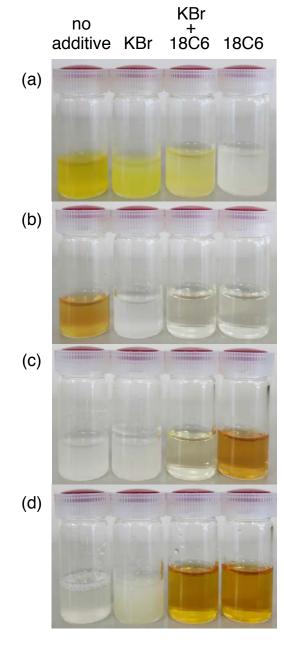
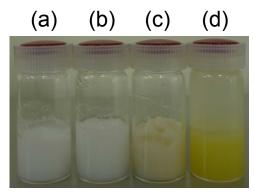


Fig. S1. Use of quaternary onium hydroxides. Conditions: (a) cellulose (20 mg), 40% TMAH (2 mL), KBr (100 mM) and/or 18C6 (1.0 M), room temperature, 24 h. (b) cellulose (20 mg), 40% BTAMH (2 mL), KBr (100 mM) and/or 18C6 (1.0 M), room temperature, 24 h. (c) cellulose (20 mg), 40% TEAH (2 mL), KBr (100 mM) and/or 18C6 (1.0 M), room temperature, 24 h. (d) cellulose (200 mg), 40% TBPH (2 mL), KBr (100 mM) and/or 18C6 (2.0 M), room temperature, 24 h. (d) h.



[B] Control experiments for the cellulose dissolution.

Fig. S2. A mixture of cellulose without TBAH. Conditions: (a) cellulose (200 mg), water (2 mL). (b) cellulose (200 mg), 18C6 (2.0 M), water (2 mL). (c) cellulose (200 mg), 40% NaOH (2.0 mL), 18C6 (2.0 M). (d) cellulose (200 mg), 40% KOH (2 mL), 18C6 (2.0 M), room temperature, 24 h.

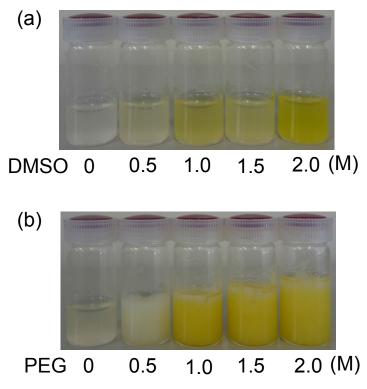


Fig. S3. The effect of DMSO or PEG. Conditions: cellulose (200 mg), 40% TBAH (2 mL), (a) DMSO or (b) PEG (concentration indicated above), room temperature, 24 h. The concentration of PEG is calculated on the basis of the monomer unit.