# Rapid self-healable poly(ethylene glycol) hydrogels formed by selective metal-phosphate interactions

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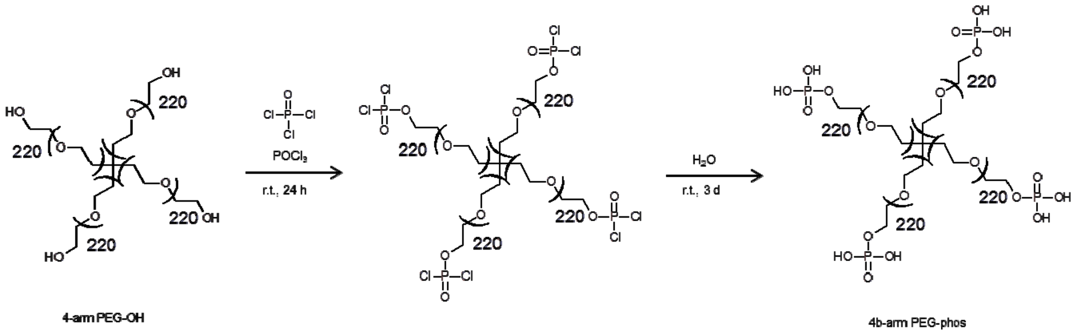
## Supporting Information

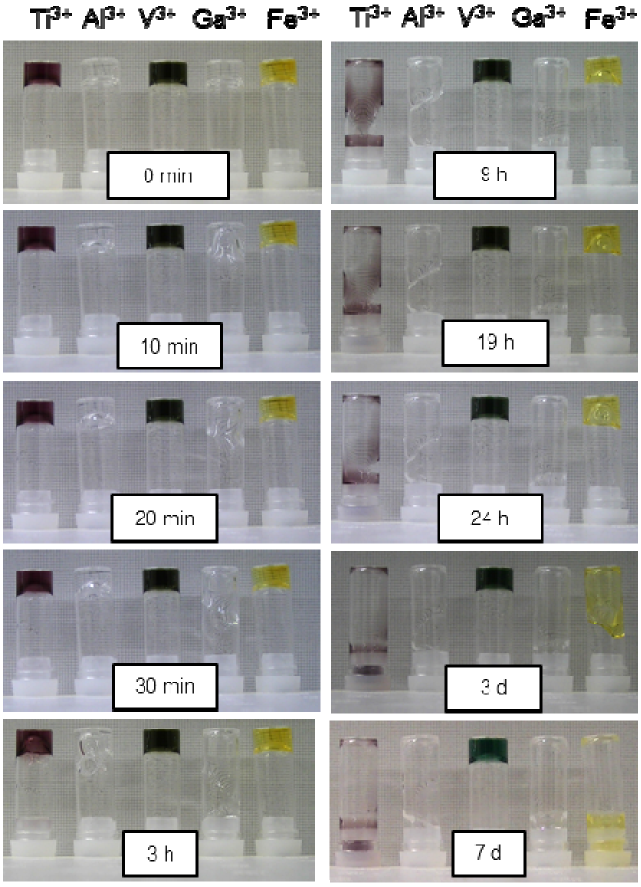
**1. Materials**

All ions used in this study, KCl(> 85.0%), $YCl_3$(99.9%), $FeCl_2$(99.0~102.0%), $VCl_3$ (99.%), $GaCl_3$(99.9%), $TiCl_3$ aqueous solution(20 w/w%), $TiCl_4$(99.0%), $MnCl_2$ (99.0%), $PdCl_2$(98.0%), $GdCl_3$(99.9%), $PbCl_2$(99.5%), NaCl(99.5%), $CrCl_3$(99.5%), $BaCl_2$(99.0%), $AlCl_3$(98.0%), $NiCl_2$(98.0%), $FeCl_3$(99.0%), $CaCl_2$(95.0%), and phosphoryl chloride(99.0%) were purchased from Wako pure chem. co. (Osaka, Japan) and used as received. Diisopropyl amine (98.0%) was also purchased from Wako pure chem. co. (Osaka, Japan) and dehydrated by KOH. Hydroxyl terminated two-arm poly(ethylene glycol) (2-arm PEG, Mn = 6,000) and hydroxyl terminated 4-arm poly(ethylene glycol) (4-arm PEG, Mn = 40,000) were kindly provided by NOF corporation (Tokyo, Japan). 2-arm PEG and 4-arm PEG were purified by precipitation before use. Briefly, the polymers were dissolved in chloroform (15.0 w/v. %) and dripped into *n*-hexane. After decantation, the precipitated polymer was filtered by vacuum filtration using a 5.0 μm pore membrane. The purified PEG was dried in a desiccator for 12 h.

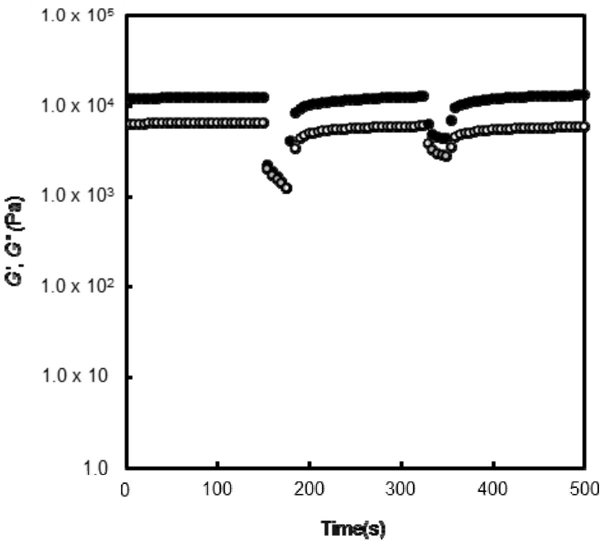
2. Scheme S1: Synthesis of four-arm star PEG with phosphate end groups (4-arm PEG phos).



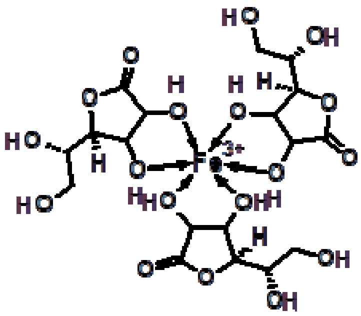
3. Figure S1: Stability test of 4-arm PEG phos solutions (5 w/v%) crosslinked by various metal ions (1 M).



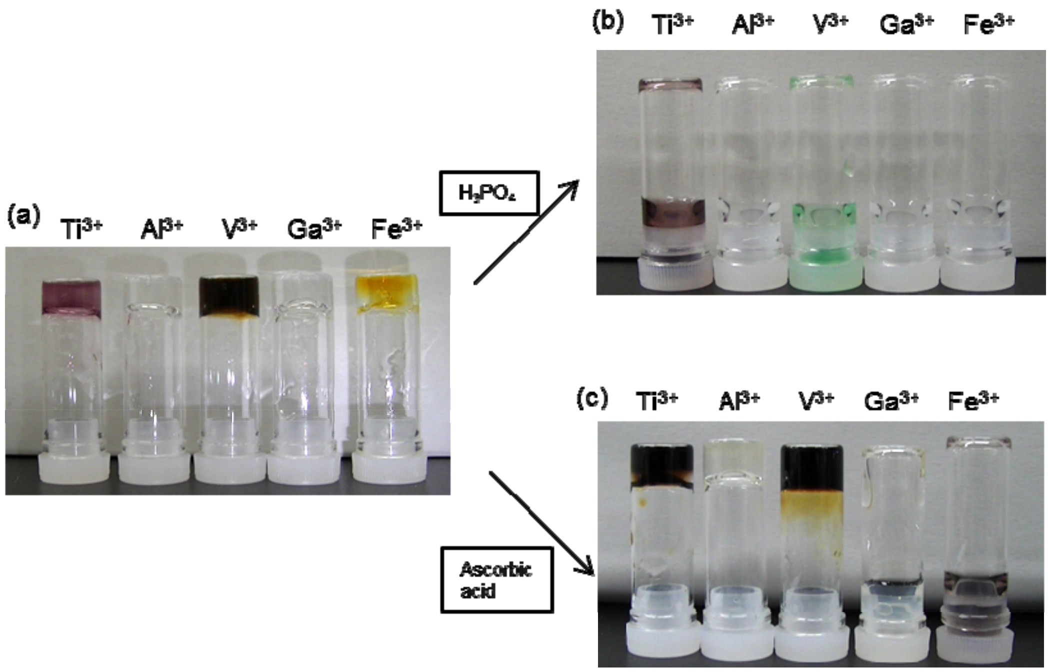
4. Figure S2: Rheological properties of hydrogels. G' (closed) and G'' (open) values of 4-arm PEG-phos with $Ga^{3+}$ in continuous step strain measurement at a constant frequency of 10 Hz at room temperature. Gel was swept from 1% to 50% strain, and then back to 1% strain.



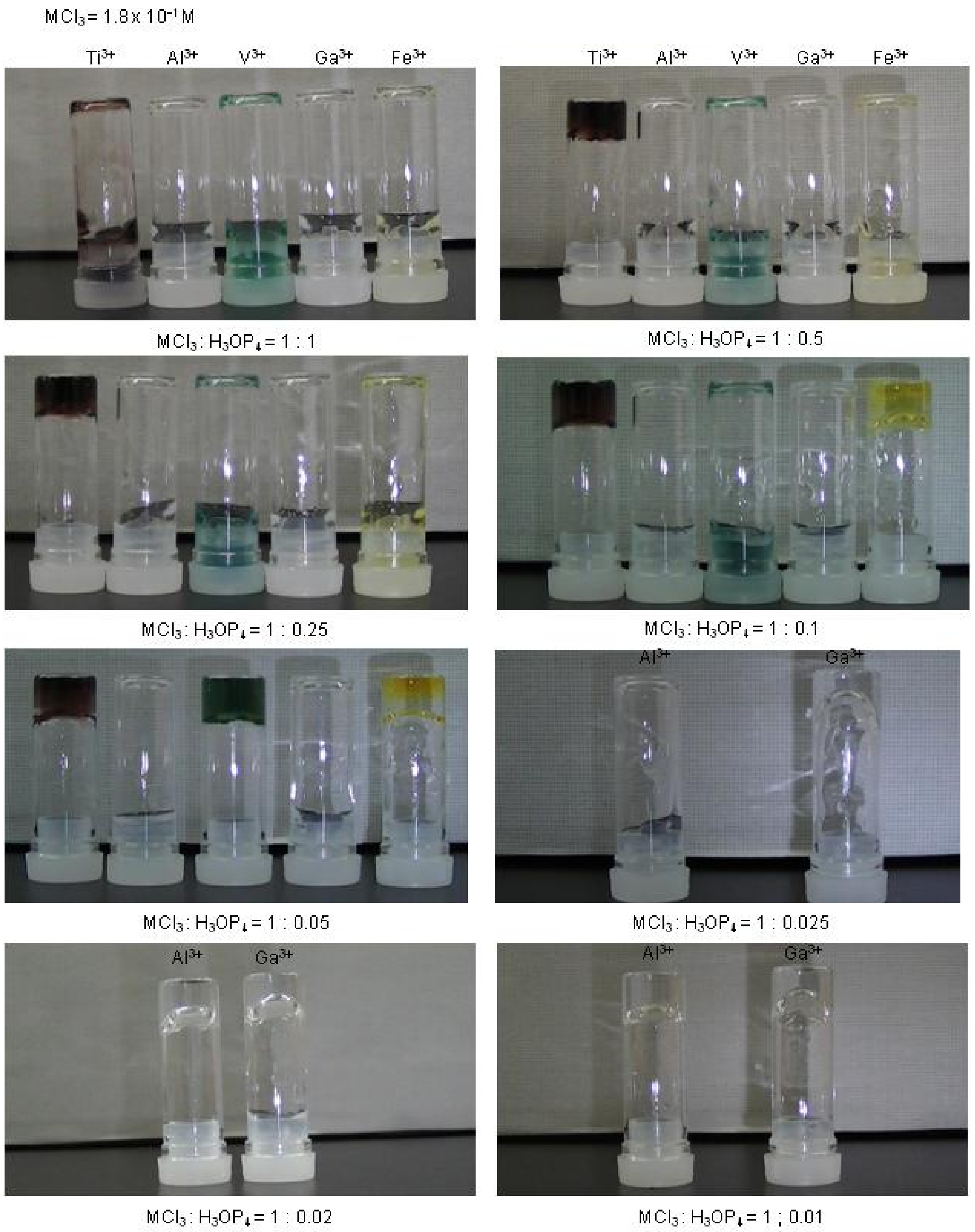
5. Figure S3: Schematic illustration of coordination bond between $Fe^{3+}$ and ascorbic acid.



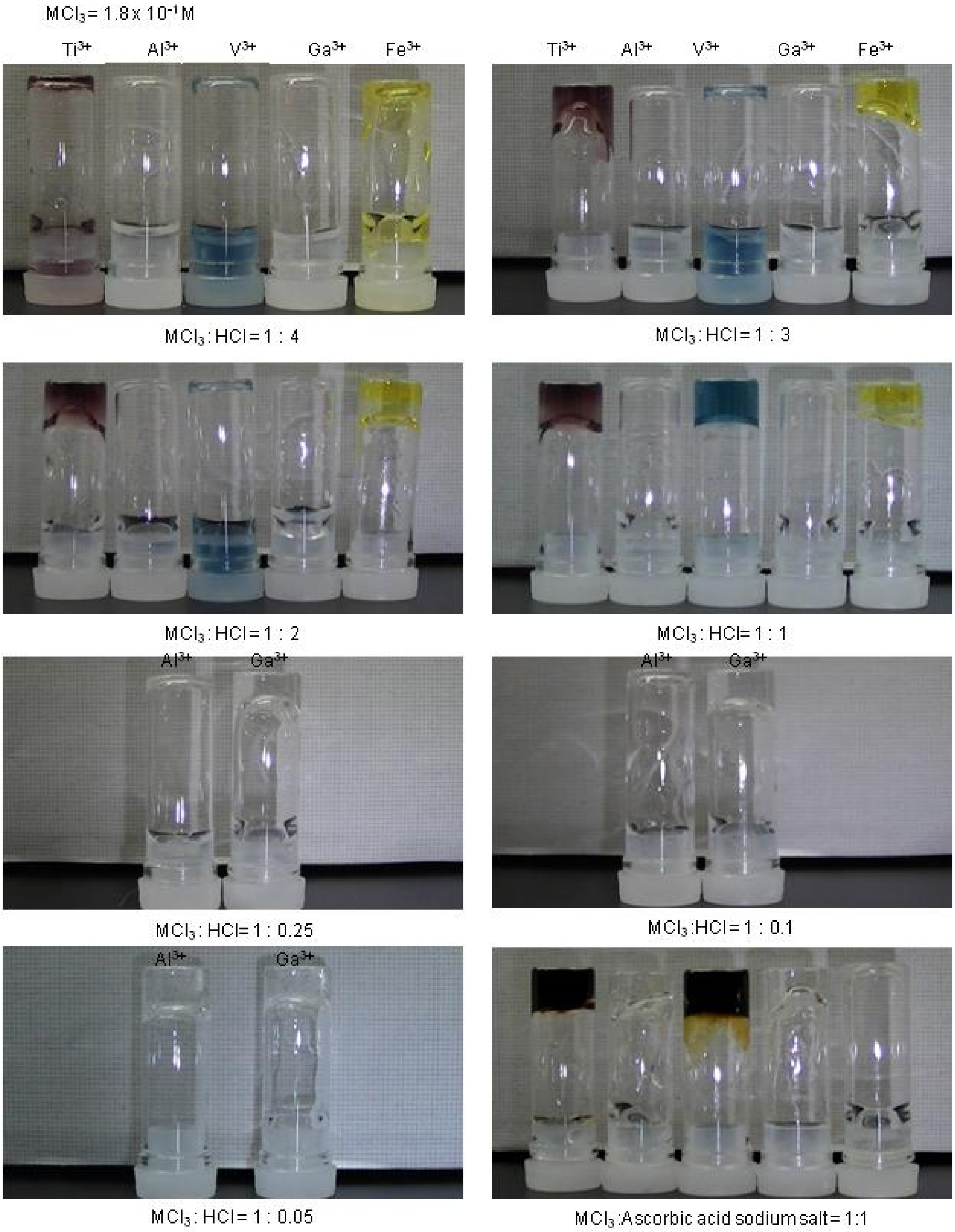
6. Figure S4: Competitive assays. 4-arm PEG-phos was gelated by $Ti^{3+}$, $Al^{3+}$, $V^{3+}$, $Fe^{3+}$, $Ga^{3+}$, and $Fe^{3+}$. Then, $H_3PO_4$ (a) and ascorbic acid (b) aqueous solution (1M) was added to the gels.



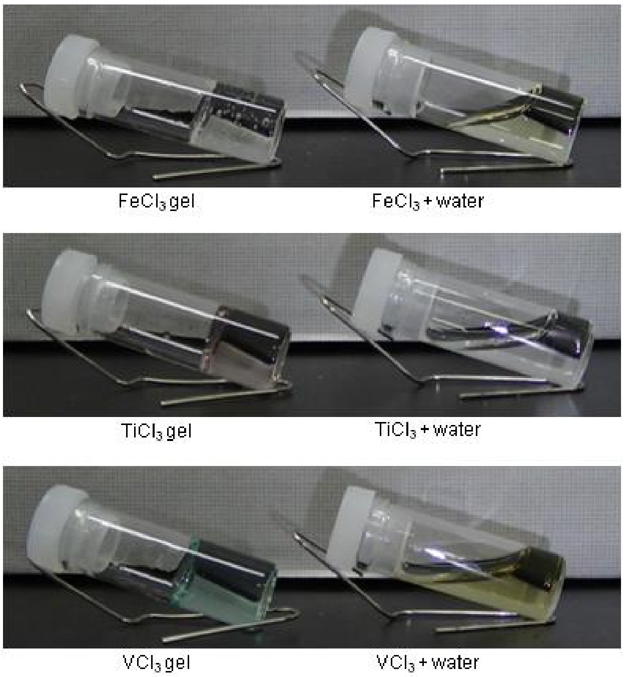
7. Figure S5: Effect of $H_3PO_4$ concentrations on hydrogel formation. The concentration of metal chloride ($MCl_3$) was fixed at $1.8 \times 10^{-1}$ M



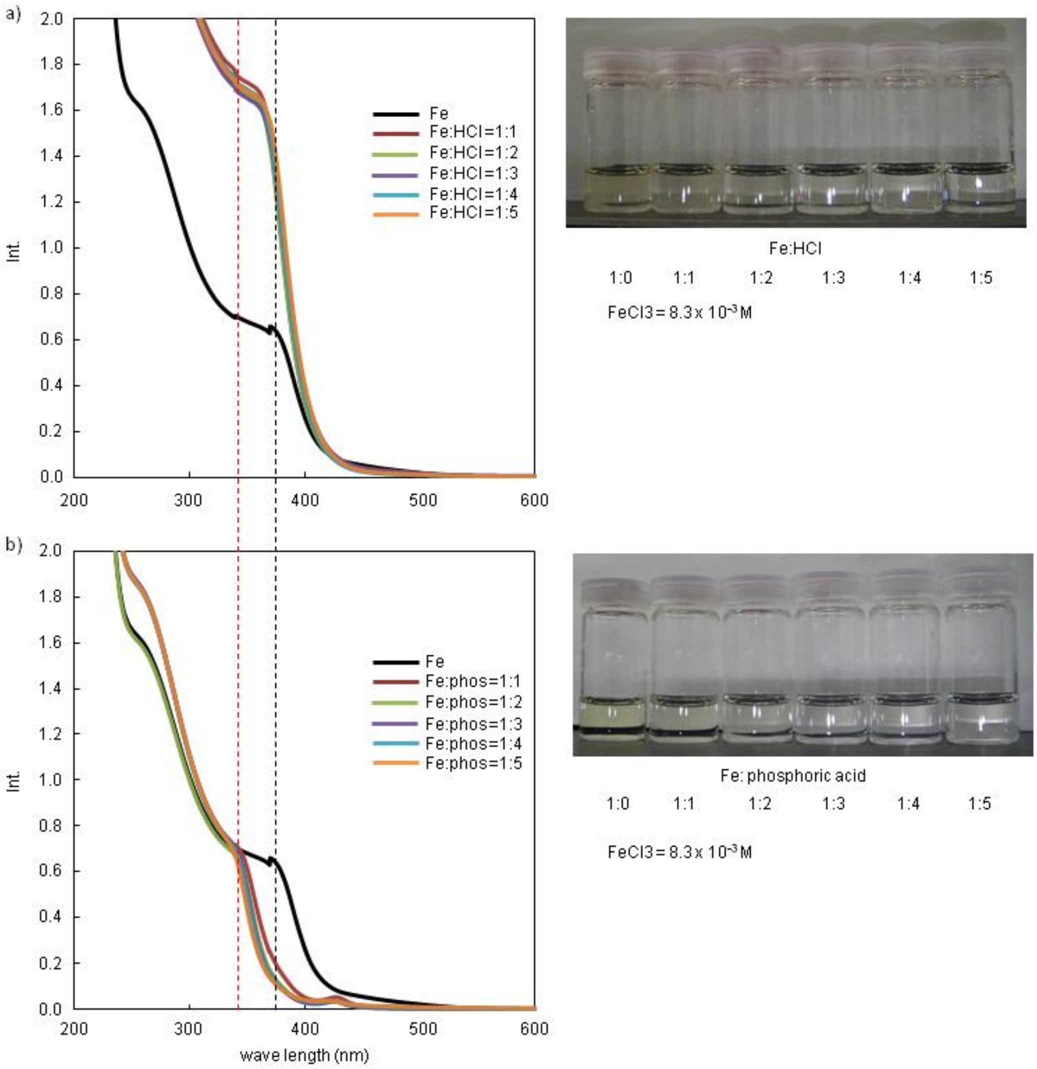
8. Figure S6: Effect of HCl or ascorbic acid sodium salt concentration on hydrogel formation. The concentration of metal chloride ($MCl_3$) was fixed at $1.8 \times 10^{-1}$ M



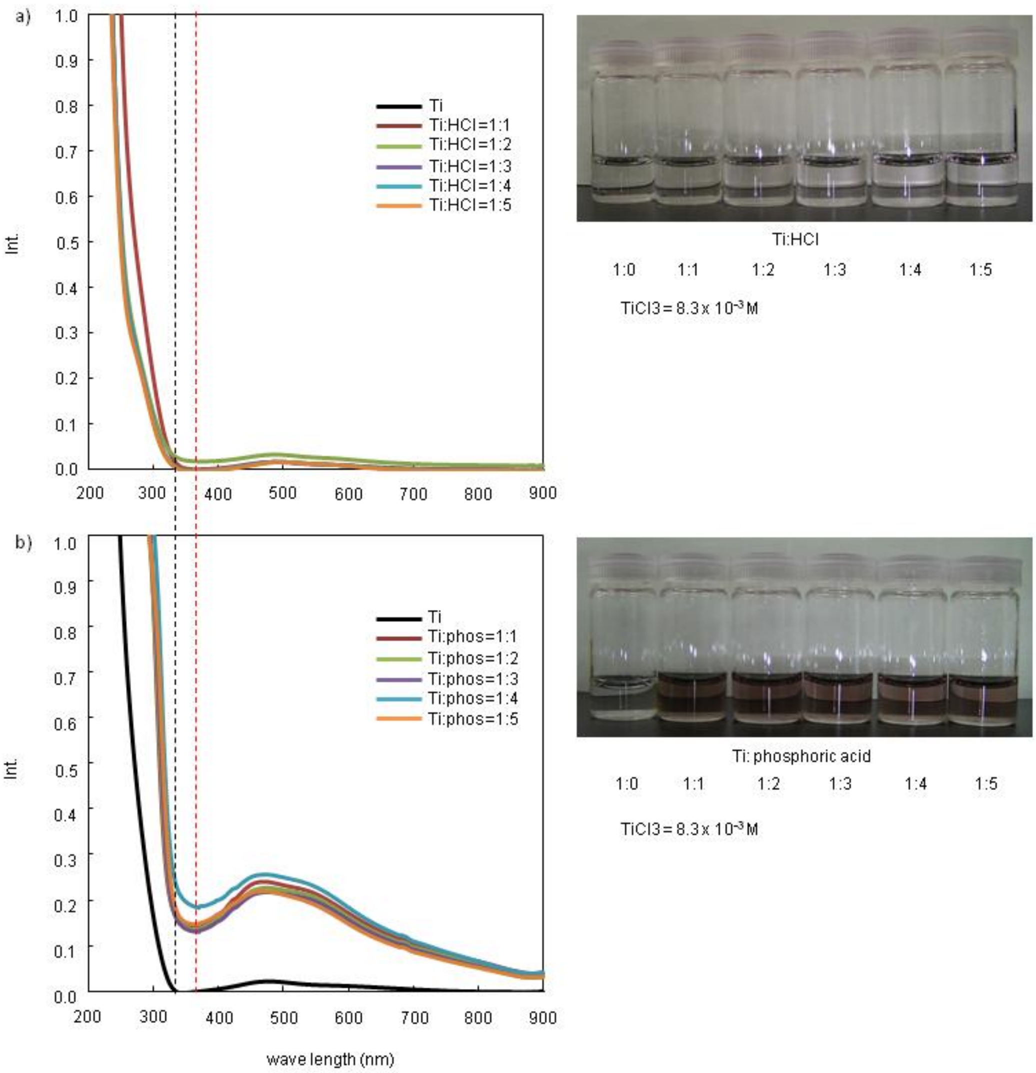
9. Figure S7: Color changes of metal ion solutions before and after mixing with 4 arm PEG-phos. The concentrations of metal chloride solution and 4-arm PEG-phos were 6.0 x $10^{-2}$ M and 10 wt%, respectively.



10. Figure S8: Optical observation of $FeCl_3$ solutions with HCl (a) and $H_3PO_4$ (b). The concentration of $FeCl_3$ was fixed at 8.3 x $10^{-3}$ M.



11. Figure S9: Optical observation of $TiCl_3$ solutions with HCl (a) and $H_3PO_4$ (b). The concentration of $TiCl_3$ was fixed at 8.3 x $10^{-3}$ M.



12. Figure S10: Optical observation of $VCl_3$ solutions with HCl (a) and $H_3PO_4$ (b). The concentration of $VCl_3$ was fixed at $8.3 \times 10^{-3}$ M.