Electronic Supplementary Material (ESI) for Soft Matter

Visualization of complexation between chloride anion and anion receptors using volume change of polyelectrolyte gels in organic solvents

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1. General

Tri-(*n*-hexyl)amine, 4-(chloromethyl)styrene, azobisisobutyronitrile (AIBN), styrene and divinylbenzene were purchased from Tokyo Chemical Ind. Co. Styrene was purified by distillation before used. All solvents were purchased from some commercial suppliers and were used without further purification. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (**NaTFPB**) was synthesized according to the reported methods.[1] Compoound **1** and **2** were synthesized according to the reported methods.[2] ^{1}H NMR spectra were measured on a Bruker AV300 and a JEOL JNM-AL300 apparatus. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer and a Bruker Daltonics autoflex III.

2. Preparation of ionic monomers 1 and 2

Synthesis of compound 1

A mixture of tri-(*n*-hexyl)amine (5.40 g, 20.0 mmol) and 4-(chloromethyl)styrene (9.16 g, 60.0 mmol) and DMF (40 ml) was stirred at 60 °C for 48 h under Ar atmosphere. The solvent was removed by a rotary evaporator, and the viscous liquid was purified by reprecipitation into excess amount of hexane to yield **1** as a white powder (7.6 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard, r.t.)□= 0.89(t, *J*=6.3 Hz, 9H $NCH_2CH_2CH_2CH_2CH_2\mathit{CH_3}$), 1.28(m, 18H, $NCH_2CH_2\mathit{CH_2CH_2CH_2}CH_3$), 1.77(m, 6H, $NCH_2\mathit{CH_2}CH_2CH_2CH_2CH_3$), 3.32(m, 6H, $N\mathit{CH_2}CH_2CH_2CH_2CH_2CH_3$), 4.99(s, 2H, $N\mathit{CH_2}C_6H_4CHCH_2$), 5.35(d, *J*=10.8, 1H, alkene*H*), 5.82(d, *J*=17.7, 1H, alkene*H*), 6.71(dd, *J*=10.8, 1H, alkene*H*) 7.49(d, *J*=8.1, 2H, Ph*H*) 7.52(d, *J*=7.8, 2H, Ph*H*). MS (MALDI-TOF):m/z calcd for $C27H48N^+$: 386.68; found: 386.67

Synthesis of Compound 2

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (10.6 g, 12.0 mmol) and **2** (5.07 g, 12.0 mmol) was dissolved in methanol (20 mL). Water was added dropwise to the stirring solution, and white solid gradually precipitated. The resulting mixture was stirred for more 3 hours. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO_2, dichloromethane) to yield **1** as a white solid. (12.1 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard, r.t.) □= 0.88(t, *J*=6.9 Hz, 9H $NCH_2CH_2CH_2CH_2CH_2\mathit{CH_3}$), 1.32(m, 18H, $NCH_2CH_2\mathit{CH_2CH_2CH_2}CH_3$), 1.72(m, 6H, $NCH_2\mathit{CH_2}CH_2CH_2CH_2CH_3$), 2.96(m, 6H, $N\mathit{CH_2}CH_2CH_2CH_2CH_2CH_3$), 4.16(s, 2H, $N\mathit{CH_2}C_6H_4CHCH_2$), 5.43(d, *J*=10.8, 1H, alkene*H*), 5.85(d, *J*=17.7, 1H, alkene*H*), 6.70(dd, *J*=10.8, 1H, alkene*H*), 7.18(d, *J*=8.1, 2H, Ph*H*), 7.52(m, 6H, Ph*H*), 7.69(s, 8H, Ph*H*). MS (MALDI-TOF): calcd for $C_{27}H_{48}N^+$: 386.68; found: 386.67, $C_{32}H_{12}BF_4^-$ 863.21; found 862.53.; elemental analysis : calcd(%) for $C_{59}H_{60}BF_{24}N$: C 56.70, H 4.84, N 1.12; found: C 56.75, H 4.84, N 1.19

3. Anion-binding properties of R1 and R2

Binding constants of **R1** and **R2** for chloride were determined by UV absorption spectroscopic method.

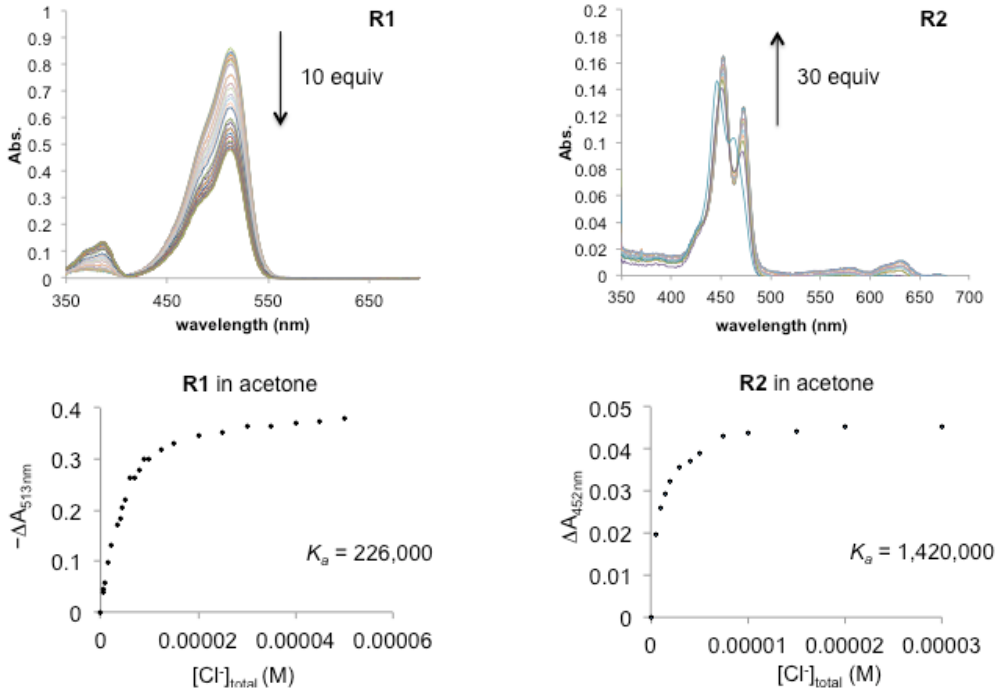

Fig. S1. UV/vis absorption spectral changes (top) and corresponding titlation plots and 1:1 fitting curves (down) of (a) **R1** (5.0×10^{-6} M), and (b) R2 (1.0×10^{-6} M) upon the addition of Cl^- as tetrabutylammonium (TBA) salts in acetone.

Table S1. Binding constants (M^{-1}) of **R1**and **R2** for chloride.

	K_a (M^{-1}) in acetone	K_a (M^{-1}) in CH_2Cl_2
R1	226,000	360,000
R2	1,420,000	2,200,000

4. Change of swelling degrees of EG-Cl in the presence of anion receptors and TBACl.

We measure the change of swelling degrees of **EG-Cl** in the presence of anion receptors (**R1** and **R2**) or tetrabutylammonium chloride (**TBACl**) in acetone.

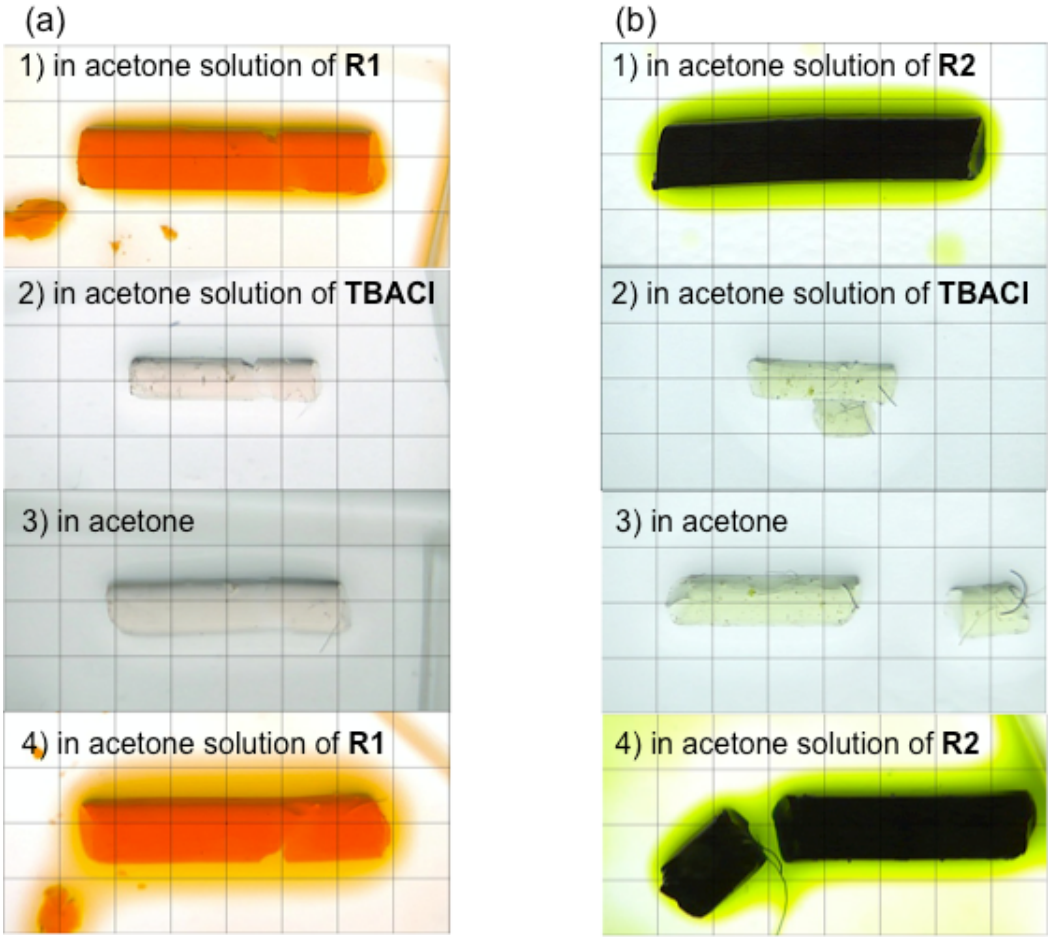

Fig. S2. Photographic images of **EG-Cl** upon the addition of a) **R1** in acetone, b) **R2** in acetone: 1) in 1 mM anion receptor solution, 2) in 10 mM **TBACl** solution, 3) in acetone, and 4) in 1 mM anion receptor solution.

References

1. D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 3810-3814.
2. K. Iseda, M. Ohta, T. Ono and K. Sada, *Soft Matter*, 2011, **7**, 5938-5940.