Electronic Supplementary Information (ESI)

Electrochemical sugar recognition using a ruthenium complex with boronic acid assembled on polyamidoamine (PAMAM) dendrimer

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Synthesis method of the Ru complex

$[Ru^{III}(acac)\}_2(4\text{-Bpy})(4\text{-Cpy})]Cl$ was synthesized as follows. Isonicotic acid (0.47 g, 2.3 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxabororan-2-yl)pyridine (0.28 g, 2.3 mmol) were added to a solution of $[Ru(acac)_3]$ (1.00 g, 2.3 mmol) in a mixed solvent of ethanol(50 cm^3)/H_2O (5 cm^3). Then, the solution was refluxed at 80 °C under argon for 10 min. After cooling, 5 cm^3 of acetone and 0.45 g of Zn powder (activated by 1 mol dm^{-3} HCl solution and then washed with water) were added to the solution. The solution was again refluxed under argon for 40 min. The solvent was then evaporated off and the residue was purified on the ODS column using a mixture of MeOH/H_2O (2:1 v/v%) as the eluent. The obtained purple crystals were stirred in a mixture of acetonitrile/H_2O (1:1 v/v%) for 24 h in order to remove pinacole as a protection group. The yield was 8% based on Ru. FAB^+ Mass. *m/z* 544 (M^+). Anal. Found: C, 42.77; H, 4.79; N, 4.68%. Calcd. for $C_{21}H_{25}O_8N_2BRu+1.5H_2O$: C, 42.75; H, 4.78; N, 4.75%.

Condition of the electrochemical measurements

The voltammetric measurements were made by means of a BAS 100B/W electrochemical workstation attached to a personal computer from Bioanalytical Systems (BAS). All the measurements were carried out at 25.0 °C. A glassy carbon disk of diameter 3.0 mm from BAS was used as the test electrode and a spiral platinum wire was used as the counter electrode. All of the potentials were measured against an aqueous Ag|AgCl (3 mol dm^{-3} NaCl aqueous solution) reference electrode from BAS. The reference electrode was connected to the test solution through a salt bridge with Vycor glass plug filled with supporting electrolyte solution. The measurement conditions for DPV : pulse amplitude ; 50mV, pulse width ; 60 ms, sample width ; 20 ms, scan rate ; 4 mV s^{-1}.

Detection limit

The limit of detection (LOD, 3σ) based on the potential for $[Ru^{II}(acac)\}_2(4\text{-Bpy})(4\text{-Cpy})]$/G2 dendrimer complex determined by the linear part in Fig. 5 was 1.5×10^{-3} mol dm^{-3}, if the resolution of the potential is 1 mV. However, the LOD depends on the pH of the solution. In general, the dissociation constants of organic boronic acids are very small, *e.g.*, 1.97×10^{-10} mol dm^{-3} for phenyl boronic acid in 25% EtOH solution. In addition, because the proton dissociation of boronic acid in $[Ru^{III}(acac)\}_2(4\text{-Bpy})(4\text{-Cpy})]^+$ occurs at pH above 10, higher sensitivity should be expected in basic solution.

Furthermore, the decreased currents in Fig. 3 showed a similar curve as that in Fig. 5 a(Fig. S5). Because the current resolution is very high (current measurement of nA level using a general-purpose potentiostat is easy), the LOD based on the current will be in the order of μmol dm^{-3}.

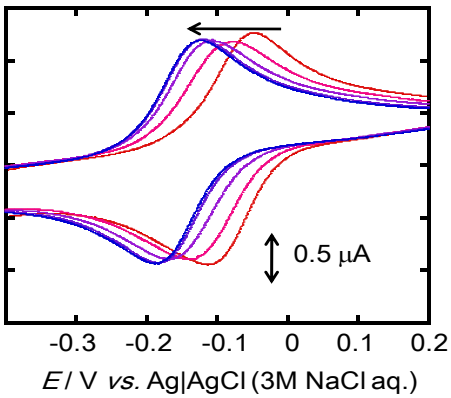

Fig. S1 The shifts of cyclic voltammogram of $[Ru^{II}(acac)\}_2$ (4-Bpy) (4-Cpy)] measured after 5 min from the addition of G2 dendrimer (0, 0.25, 0.50, 0.75, 1.00, 1.25 eq.) in 0.1 mol dm^{-3} $NaClO_4$/(H_2O:MeOH = 8:2) at GCDE (ϕ = 3 mm) at 25 °C. Scan rate = 100 mV s^{-1}.

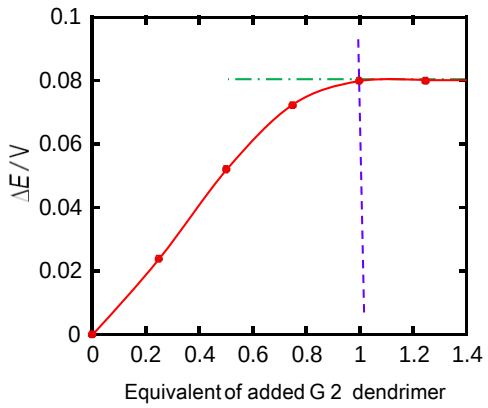

Fig. S2 The peak potential shifts of DPV of $[Ru^{II}(acac)\}_2$ (4-Bpy) (4-Cpy)] measured after 5 min from the addition of G2 dendrimer in 0.1 mol dm^{-3} $NaClO_4$/(H_2O:MeOH = 8:2) at GCDE (ϕ = 3 mm) at 25 °C.

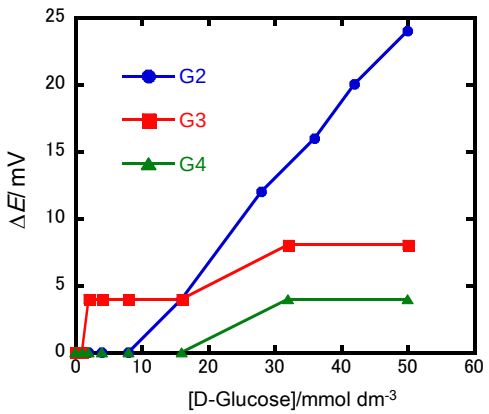

Fig. S3 Peak potential shift of DPV of $[Ru^{II}(acac)\}_2$ (4-Bpy) (4-Cpy)] containing one equivalent G2, G3, or G4 dendrimer by the addition of D-glucose.

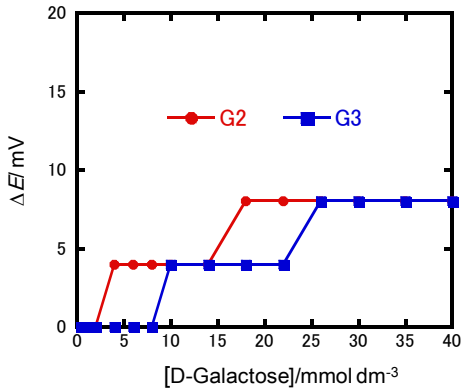

Fig. S4 Peak potential shift of DPV of $[Ru^{II}(acac)\}_2$ (4-Bpy) (4-Cpy)] containing one equivalent G2and G3dendrimer by the addition of D-galactose.

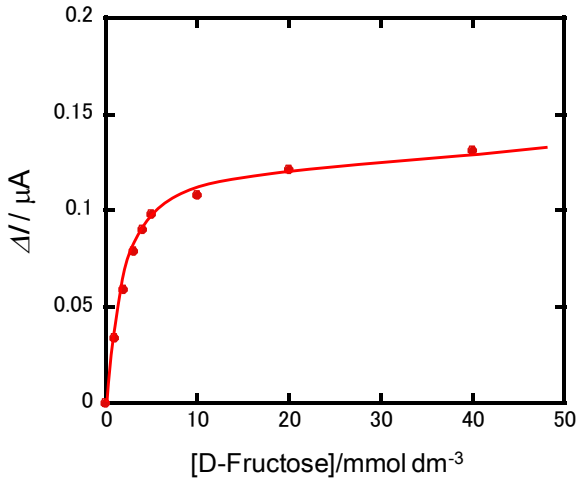

Fig. S5 The peak current shifts of DPV of $[Ru^{II}(acac)\}_2$(4-Bpy) (4-Cpy)] containing one equivalent G2 dendrimer by the addition of D-fluctose.

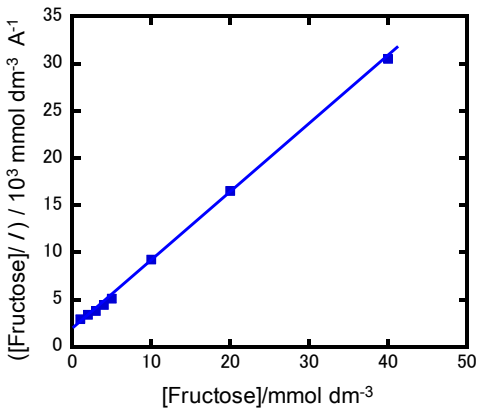

Fig. S6 The plot of ([Fructose] / *I*) *vs*. [Fructose] $[Ru^{II}(acac)\}_2$ (4-Bpy)(4-Cpy)]/dendrimer complex. *I* is the peak current of DPV.