

Electronic Supplementary Information (ESI)

Bioinspired synthesis of poly(phenylboronic acid) microgels with high glucose selectivity at a physiological pH

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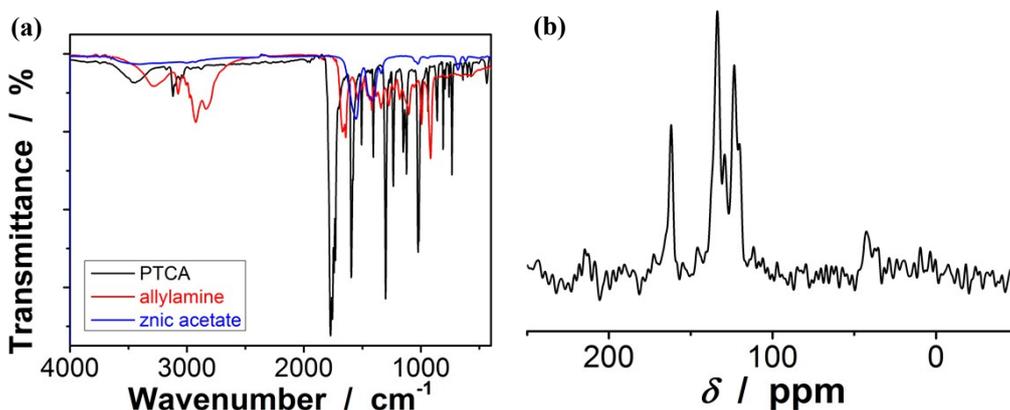


Fig. S1 (a) IR spectrum of PTCA and other compounds for the synthesis of pp-PTCDI. (b) ¹³C CP-MAS NMR spectrum of pp-PTCDI.

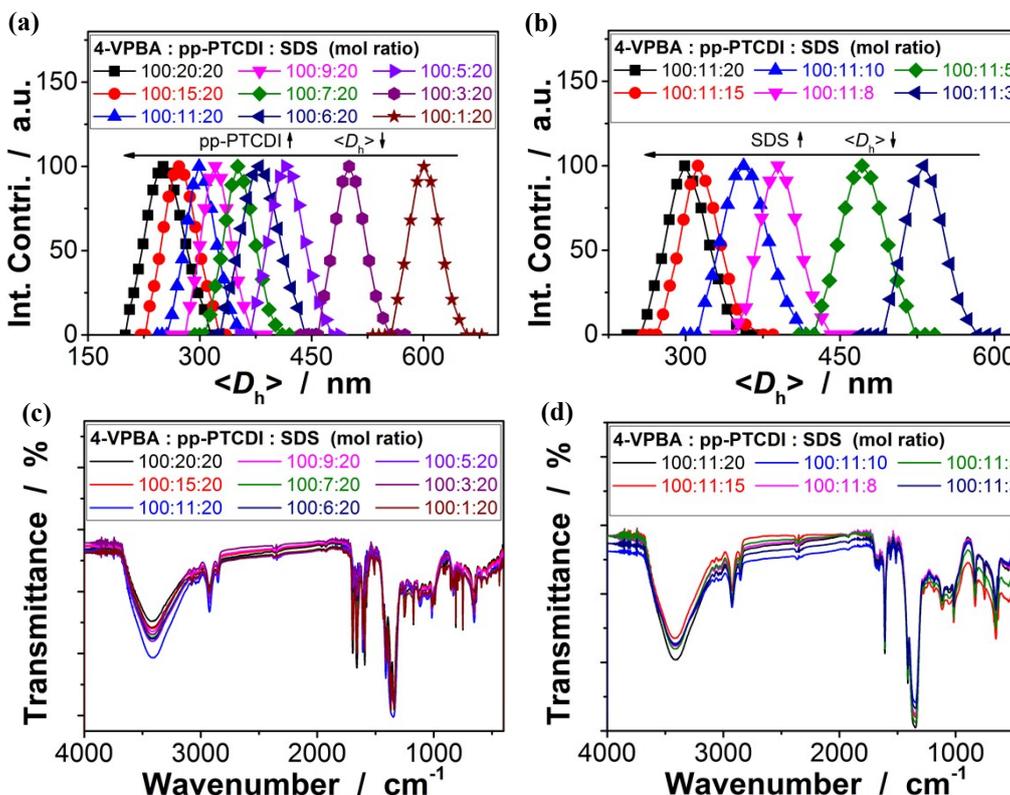


Fig. S2 DLS size distribution of the microgels synthesized with different mol ratios of 4-VPBA/pp-PTCDI/SDS. To show the effect of the feeding amount of (a) pp-PTCDI and (b) SDS, the feeding amount of 4-VPBA was set to 5.0×10^{-4} mol. All measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C. (c,d) IR spectra of the samples.

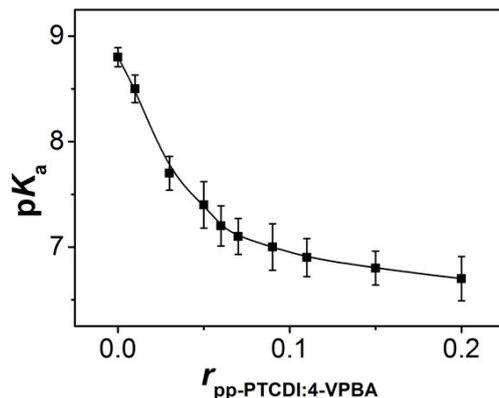


Fig. S3 The pK_a the PBA groups as a function of feeding molar ratio $r_{pp\text{-PTCDI}:4\text{-VPBA}}$ in the synthesis of the microgels. The pK_a was measured by titration, and defined as the pH corresponding to the peak position on the $\Delta\text{pH}/\Delta V\text{-}V_{\text{NaOH}}$ plot.

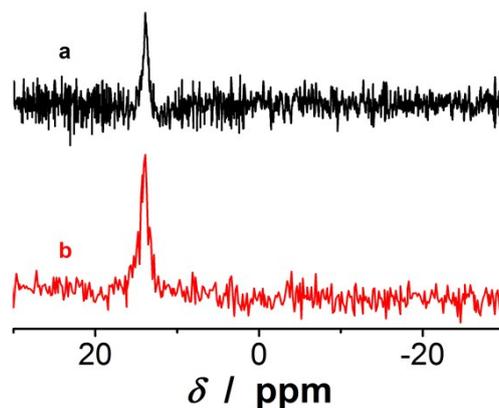


Fig. S4 ^{11}B NMR spectra of (a) a control sample synthesized with the 4-VPBA monomer using MBAAm (feeding molar ratio $r_{\text{MBAAm}:4\text{-VPBA}} = 11:100$) as a crosslinker, and (b) a mixture of this control sample and pp-PTCDI upon simple mixing. All measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C.

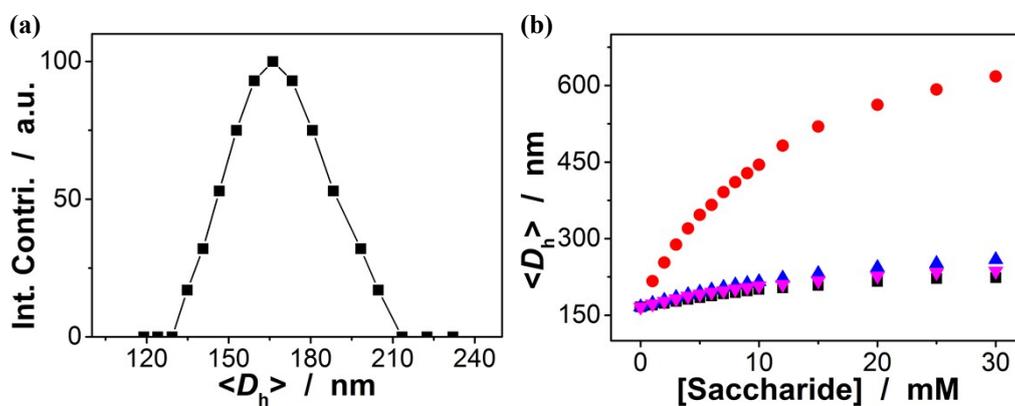


Fig. S5 (a) DLS size distribution of the control sample synthesized with the 4-VPBA monomer using MBAAm (feeding molar ratio $r_{\text{MBAAm}:4\text{-VPBA}} = 11:100$) as a crosslinker. (b) Saccharide-dependent $\langle D_h \rangle$ values of the microgels dispersed in PBS with glucose (■), fructose (●), galactose (▲), and mannose (▼). DLS measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C.

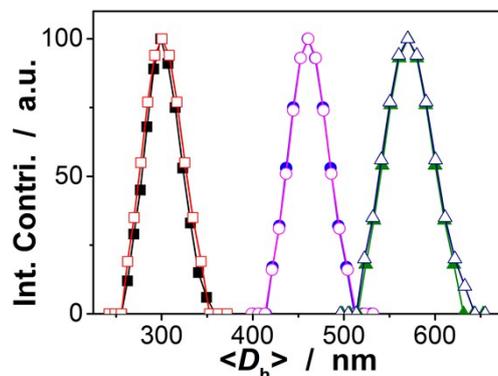


Fig. S6 DLS size distribution of the microgels ($10.0 \mu\text{g/mL}$) dispersed in the solutions with $[\text{Glu}] = 0.0 \text{ mM}$ (\blacksquare, \square), 5.0 mM (\bullet, \circ), and 30.0 mM ($\blacktriangle, \triangle$), before (solid symbols) and after (open symbols) adding/removing Glu for twenty cycles. All measurements were made in 5.0 mM PBS of $\text{pH} = 7.4$ at $25.0 \text{ }^\circ\text{C}$.

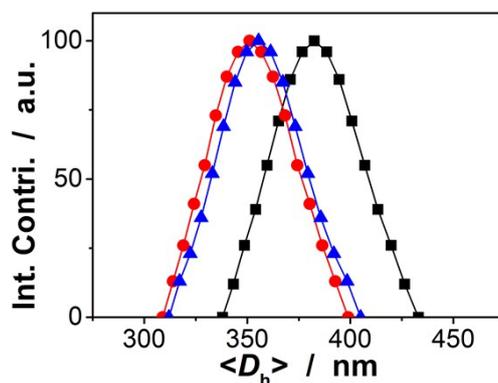


Fig. S7 DLS size distribution of the microgels ($10.0 \mu\text{g/mL}$) dispersed in the solutions with 30.0 mM fructose (\blacksquare), galactose (\bullet), and mannose (\blacktriangle). All measurements were made in 5.0 mM PBS of $\text{pH} = 7.4$ at $25.0 \text{ }^\circ\text{C}$.

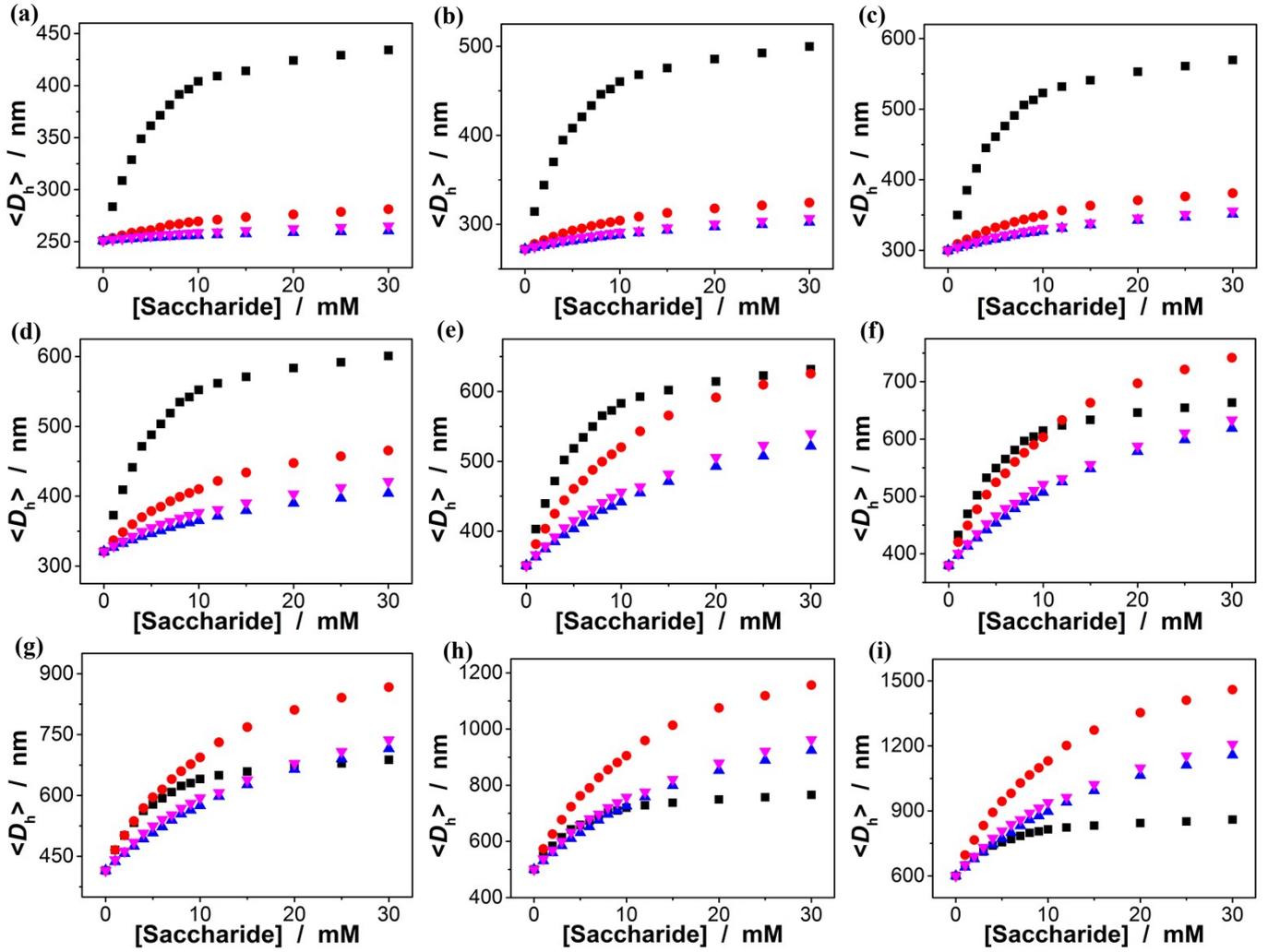


Fig. S8 Saccharide-dependent $\langle D_h \rangle$ values of the microgels dispersed in PBS with glucose (■), fructose (●), galactose (▲), and mannose (▼), showing the impact of the feeding molar ratio $r_{pp-PTCDI:4-VPBA}$ in the synthesis of the microgels: (a) 0.20; (b) 0.15; (c) 0.11; (d) 0.09; (e) 0.07; (f) 0.06; (g) 0.05; (h) 0.03; and (i) 0.01. DLS measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C.

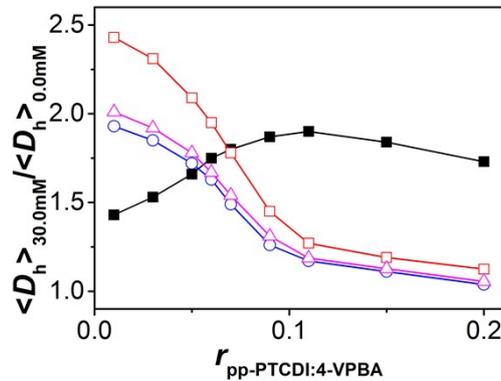


Fig. S9 The swelling ratio, $\langle D_h \rangle_{30.0mM} / \langle D_h \rangle_{0.0mM}$, as a function of feeding molar ratio $r_{pp-PTCDI:4-VPBA}$ of the microgels. DLS measurements were made in 5.0 mM PBS with glucose (■), fructose (□), galactose (○), and mannose (△) of pH = 7.4 at 25.0 °C.

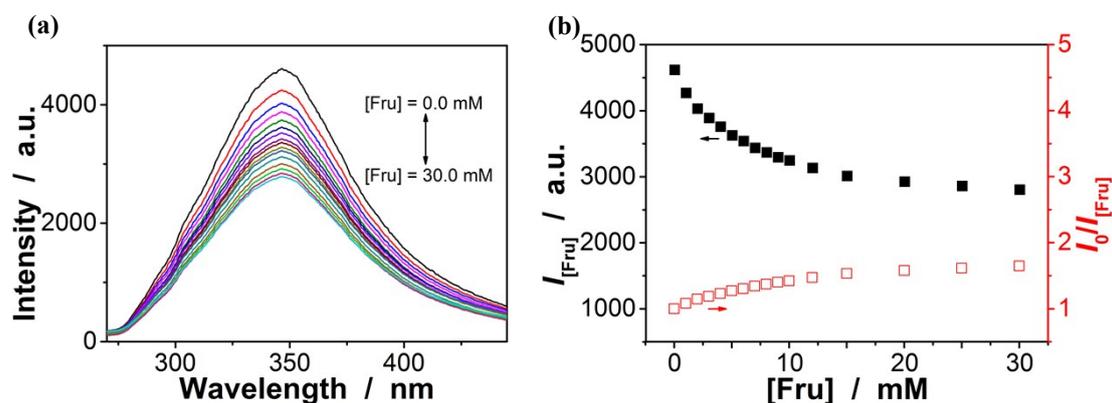


Fig. S10 [Fru]-dependent (a) PL spectra and (b) $I_{[\text{Fru}]}$ and $I_0/I_{[\text{Fru}]}$ values. All measurements were made on the microgel dispersion (10.0 $\mu\text{g}/\text{mL}$) at 25.0 $^\circ\text{C}$.

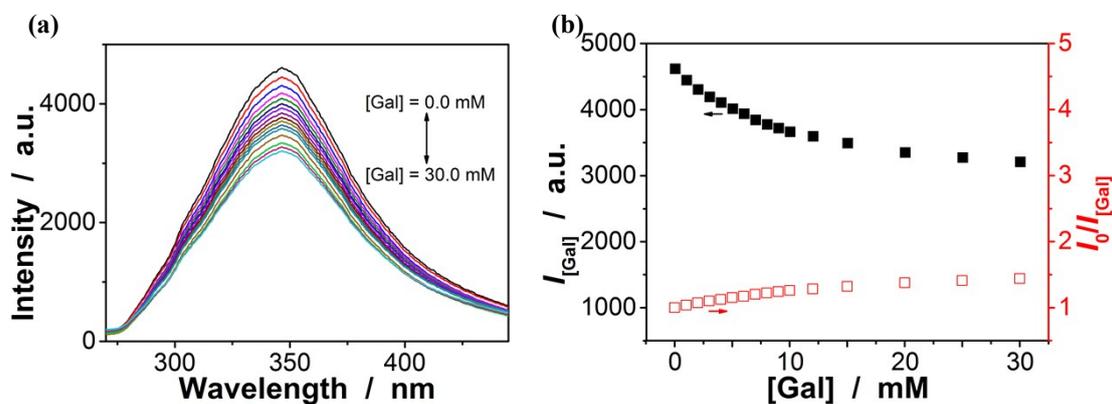


Fig. S11 [Gal]-dependent (a) PL spectra and (b) $I_{[\text{Gal}]}$ and $I_0/I_{[\text{Gal}]}$ values. All measurements were made on the microgel dispersion (10.0 $\mu\text{g}/\text{mL}$) at 25.0 $^\circ\text{C}$.

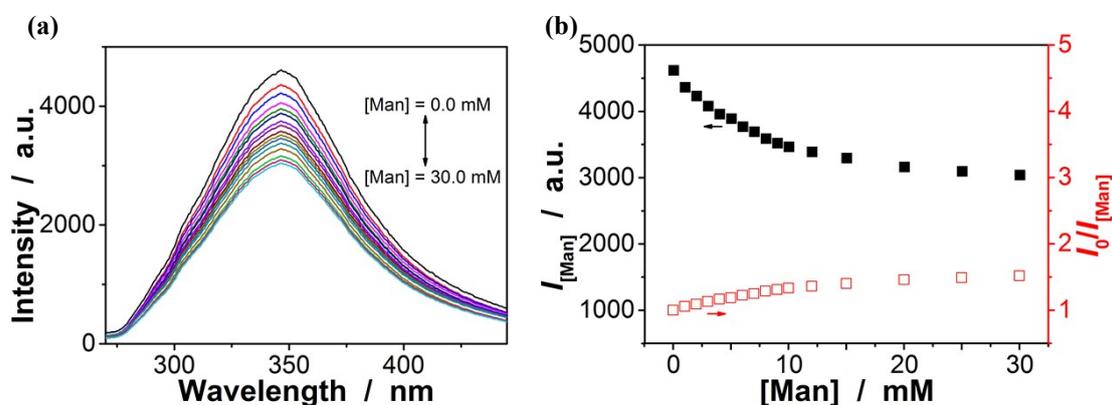


Fig. S12 [Man]-dependent (a) PL spectra and (b) $I_{[\text{Man}]}$ and $I_0/I_{[\text{Man}]}$ values. All measurements were made on the microgel dispersion (10.0 $\mu\text{g}/\text{mL}$) at 25.0 $^\circ\text{C}$.

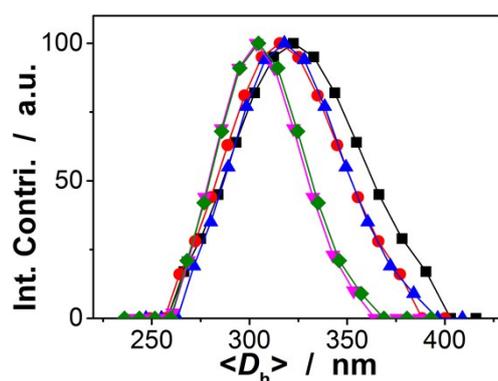


Fig. S13 DLS size distribution of the microgels in the presence of absorbed dextran ($M_r \sim 6,000$) (■), dextran ($M_r \sim 40,000$) (●), dextran ($M_r \sim 100,000$) (▲), RNase B (▼) and HSA (◆). All measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C.

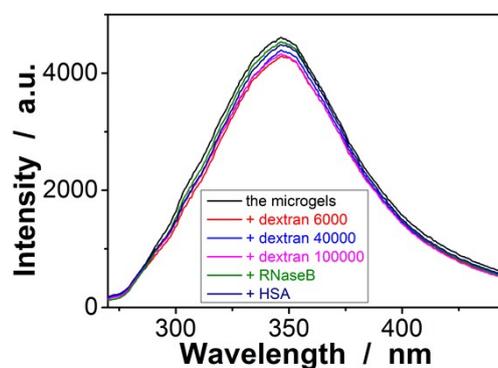


Fig. S14 PL spectra of the microgels in the presence of absorbed dextran ($M_r \sim 6,000$), dextran ($M_r \sim 40,000$), dextran ($M_r \sim 100,000$), RNase B and HSA. All measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C.

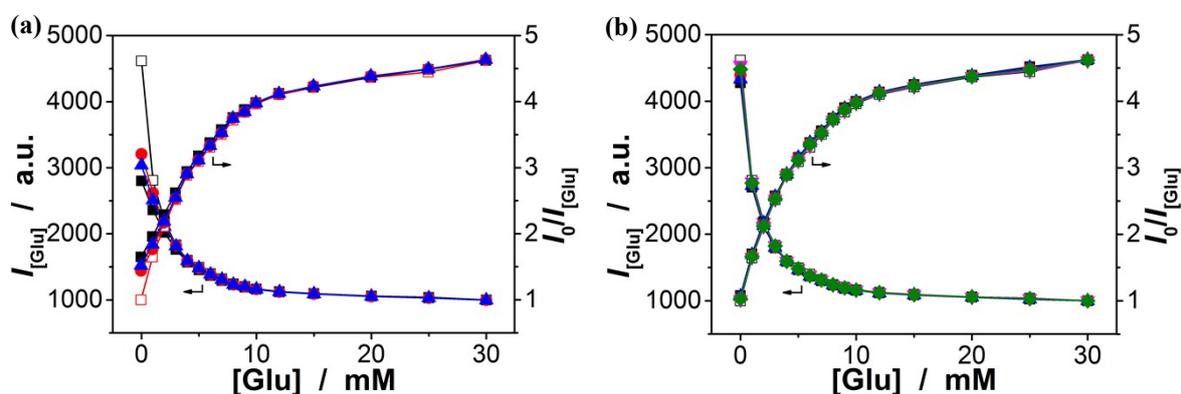


Fig. S15 [Glu]-dependent $I_{[\text{Glu}]}$ and $I_0/I_{[\text{Glu}]}$ values of SPBA microgels dispersed in PBS with in the presence of (a) 30.0 mM of fructose (■), mannose (●), or galactose (▲), and (b) absorbed dextran ($M_r \sim 6,000$) (■), dextran ($M_r \sim 40,000$) (●), dextran ($M_r \sim 100,000$) (▲), RNase B (▼) and HSA (◆). The results in the absence of those non-glucose constituents (□) are given for comparison. All measurements were made in 5.0 mM PBS of pH = 7.4 at 25.0 °C.