Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Control of Electrostatic Interaction between Molecular Beacon Aptamer and Conjugated Polyelectrolyte for Detection Range-Tunable ATP Assay

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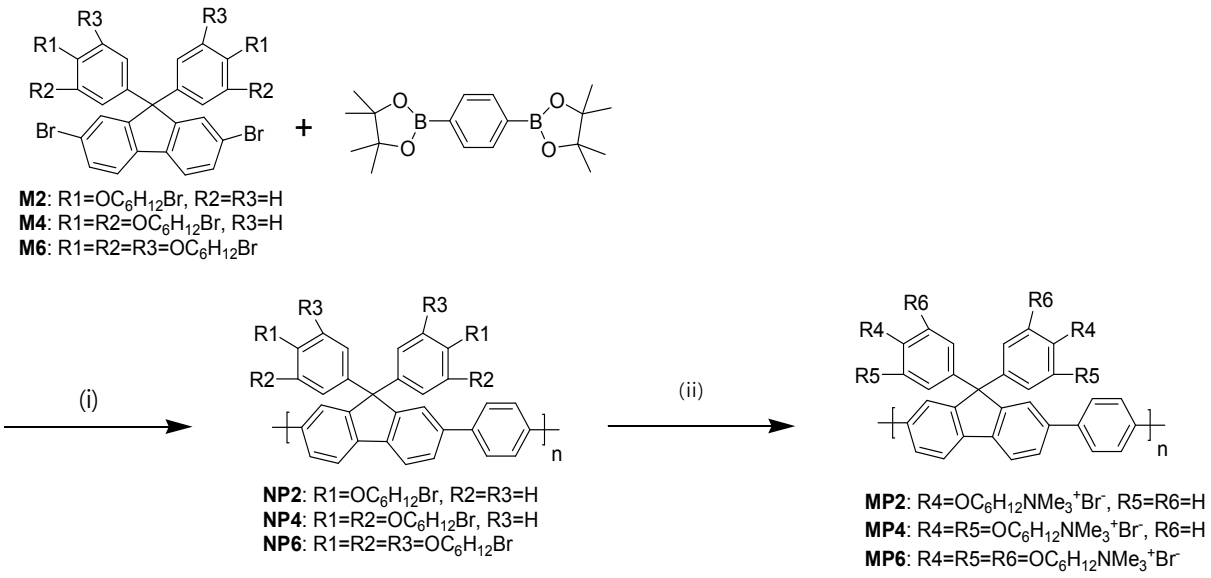


M2: R1=$OC_6H_{12}Br$, R2=R3=H
M4: R1=R2=$OC_6H_{12}Br$, R3=H
M6: R1=R2=R3=$OC_6H_{12}Br$

NP2: R1=$OC_6H_{12}Br$, R2=R3=H
NP4: R1=R2=$OC_6H_{12}Br$, R3=H
NP6: R1=R2=R3=$OC_6H_{12}Br$

MP2: R4=$OC_6H_{12}NMe_3^+Br^-$, R5=R6=H
MP4: R4=R5=$OC_6H_{12}NMe_3^+Br^-$, R6=H
MP6: R4=R5=R6=$OC_6H_{12}NMe_3^+Br^-$

Scheme S1. Synthetic routes to CPEs. Reagents and conditions: (i) $Pd(PPh_3)_4$, aliquat, toluene, 2M K_2CO_3, reflux; (ii) trimethylamine in tetrahydrofuran/methanol, room temperature, 48 h.

Table S1. Molecular weights of neutral precursor polymers.

Polymers	M_n (g/mol)[a]	M_w (g/mol)[b]	PDI
NP2	21,400	42,100	1.97
NP4	15,300	38,300	2.50
NP6	19,100	34,400	1.80

[a]Number-average molecular weight. [b]Weight-average molecular weight.

Table S2. Summary of optical properties of CPEs in Tris-HCl buffer.

MPs	λ_{abs} (nm)[a]	λ_{PL} (nm)[b]	Φ_{PL}[c] (%)	ε_{max}[d] ($M^{-1}cm^{-1}$)
MP2	379	420	35	4.5×10^4
MP4	378	421	40	5.4×10^4
MP6	374	418	70	5.6×10^4

[a]Maximum absorption wavelength. [b]Maximum PL wavelength. [c]PL quantum efficiency. [d]Molar absorption coefficient at λ_{abs}.

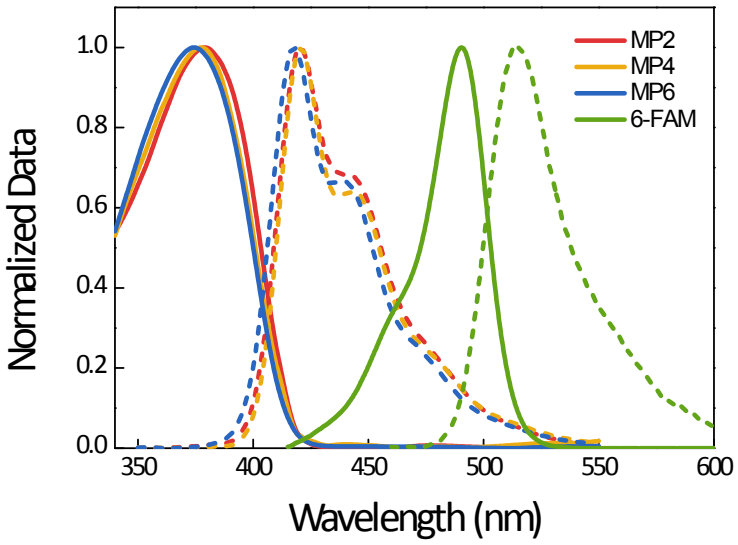


Fig S1. Absorption (solid) and PL (dashed) spectra of MPs and 6-FAM in 20 mM of Tris-HCl buffer (pH 7.4). [MPs] = 3 μM.

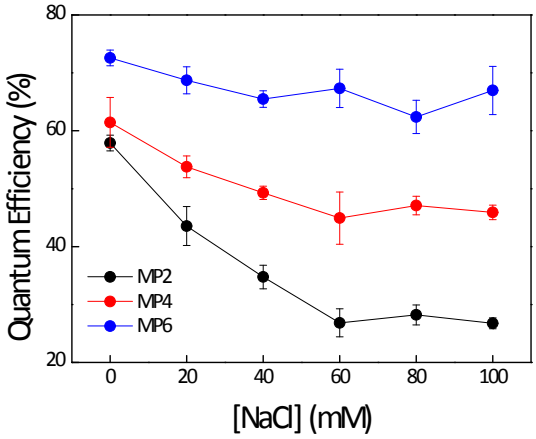
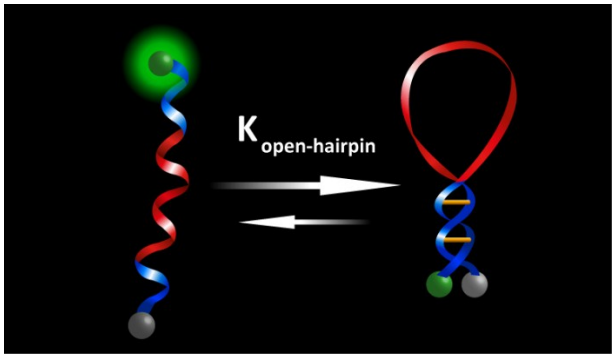


Fig S2. PL Quantum efficiency of MPs depending on [NaCl] in 20 mM of Tris-HCl buffer (pH 7.4). [NaCl] = 0~100 mM. [MPs] = 2.5 μM. Excitation at 380 nm.

Table S3. Equilibrium constants for conformational transformation of MBAs



	MBA sequence (5' - 3')[a]	ΔG^0	Equilibrium constant ($K_{open\text{-}hairpin}$)
MBA1	GCGC GCGG GGAG TATT GCGG AGGA GCGC GC	-5.8 kcal/mol	1.2×10^4
MBA2	GCGC GCGC GGGG AGTA TTGC GGAG GAGC GCGC	-9.7 kcal/mol	6.4×10^6
MBA3	GCGC GCGC GCGG GGAG TATT GCGG AGGA GCGC GCGC GC	-13.5 kcal/mol	3.5×10^9

[a]All MBA were labeled with [6-FAM] at 5' and [DABCYL] at 3' termini

*** Calculation of Gibbs free energy**

http://mfold.rna.albany.edu

The equilibrium constants for conformational change of MBAs were obtained at the above website where the standard Gibbs free energy change, ΔG°, was calculated for folding of nucleic acids with particular base sequence.

(37 ℃, $[Na^+]$ = 100 mM and $[Mg^{2+}]$ = 0 M)

*** Equilibrium Constant (K)**

$\Delta G = \Delta G^\circ + RT\ln K$

In equilibrium state, $\Delta G = 0$

$\therefore \Delta G^\circ = -RT\ln K$

$$\ln K = \Delta G^\circ / -RT$$

$$K = e^{(\Delta G^\circ / -RT)}$$

Where R is gas constant (1.9863 cal/k·mol), T is temperature (310.15 K) and G is Gibbs free energy.

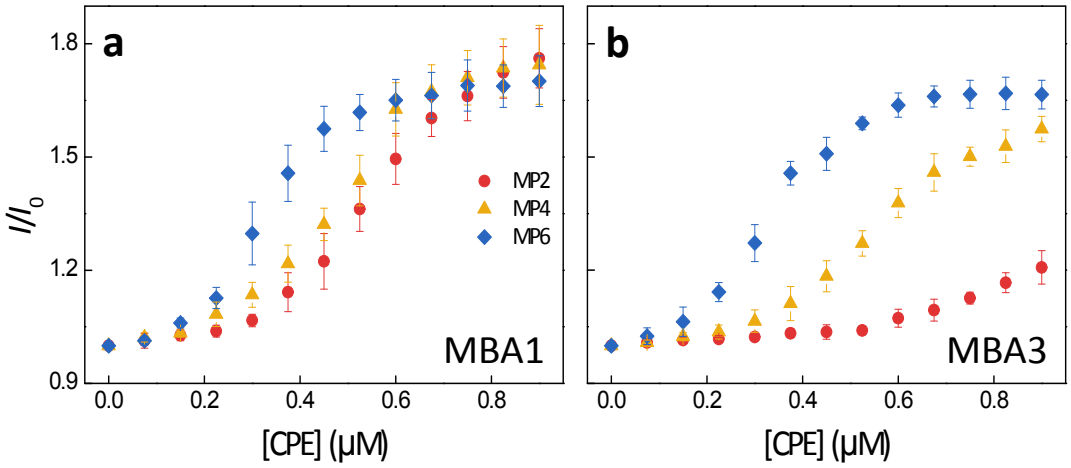


Fig S3. Comparison of fluorescence enhancement of (a) MBA1 and (b) MBA3 with increasing [MPs] = 0 ~ 0.9 μM. [MBA1] = [MBA3] = 20 nM. Excitation at 490 nm.