Supporting Information

Infrequent Metadynamics Study of Rare-event Electrostatic Channeling

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S1 Definition of Infrequent Metadynamics Basins

In the committor analysis of infrequent metadynamics, we defined 19 possible triple association basins, besides d_{246}, based on the assumption that the nearby index difference of the three indexes of d_{ijk} should not be greater than 2. For instance, d_{123}, d_{124}, d_{135} and d_{134} are possible, but not d_{125} or d_{145}. Therefore, these basins below are all assumed to be possible triple association basins: d_{123}, d_{124}, d_{134}, d_{135}, d_{234}, d_{235}, d_{245}, d_{246}, d_{345}, d_{346}, d_{356}, d_{357}, d_{456}, d_{457}, d_{467}, d_{468}, d_{567}, d_{568}, d_{578}, and d_{678}.

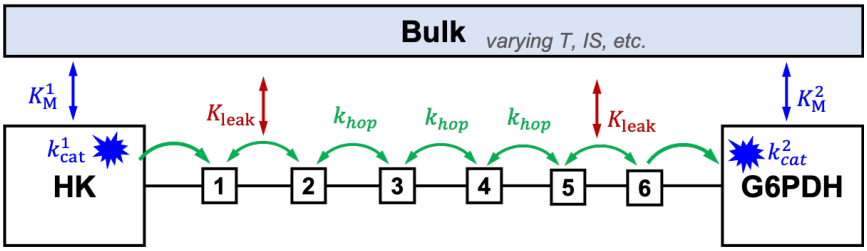

Fig. S1 Schematic of the KMC model.

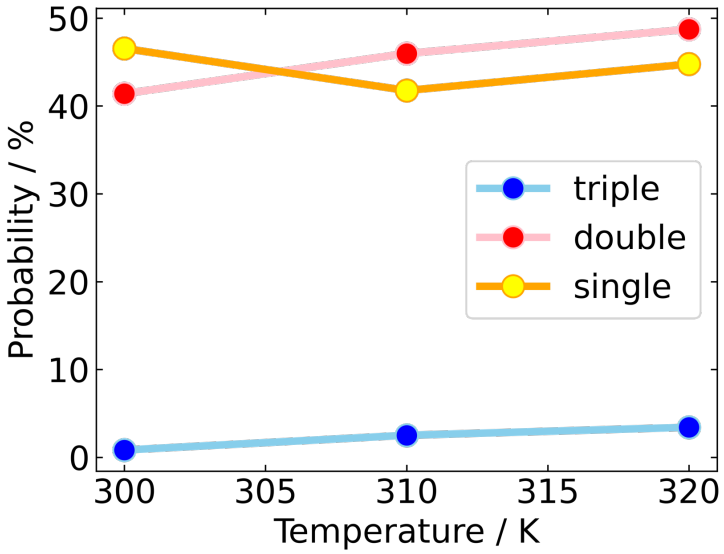

Fig. S2 Association state probability of G6P on the poly-lysine bridge.

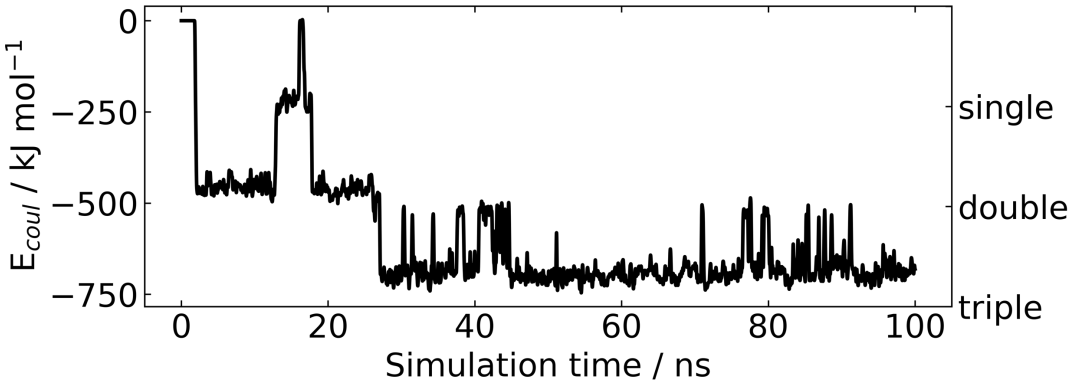

Fig. S3 Electrostatic energy between G6P and the poly-arginine bridge.

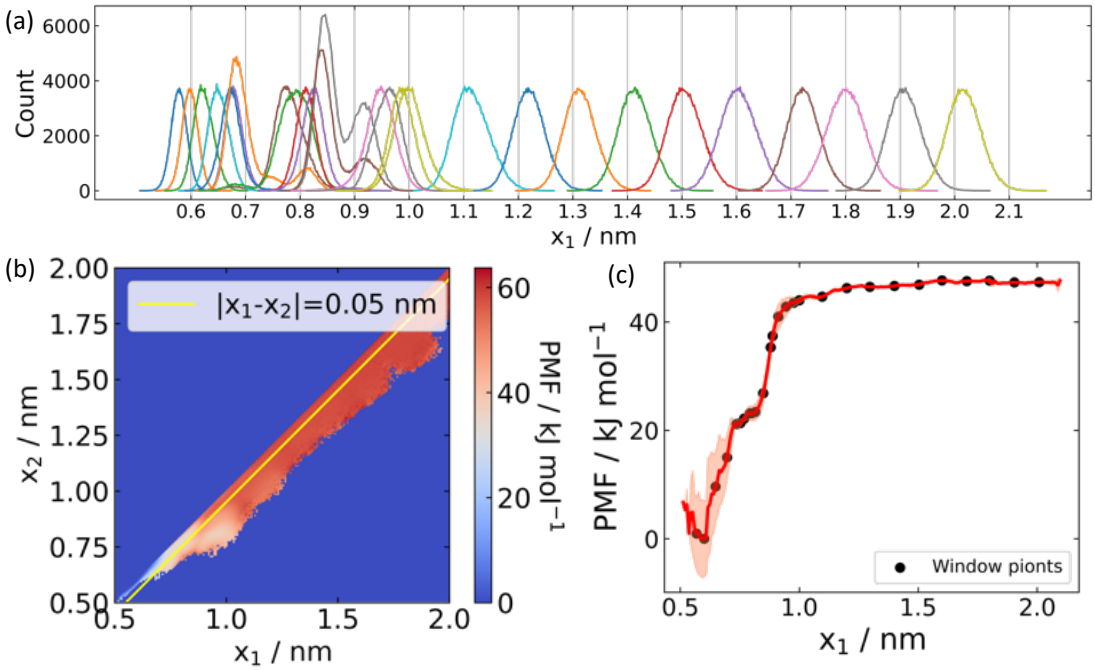

Fig. S4 (a) Example biased distribution of x_1 of all the US windows at IS = 0 mM, temperature 300 K. (b) Example 2D energy plot of G6P desorption energy from the triple association on the poly-arginine peptide. Data above the yellow cutoff line was used for calculation of the PMF. (c) The projection of desorption energy on x_1 at IS = 0 mM, temperature 300 K.

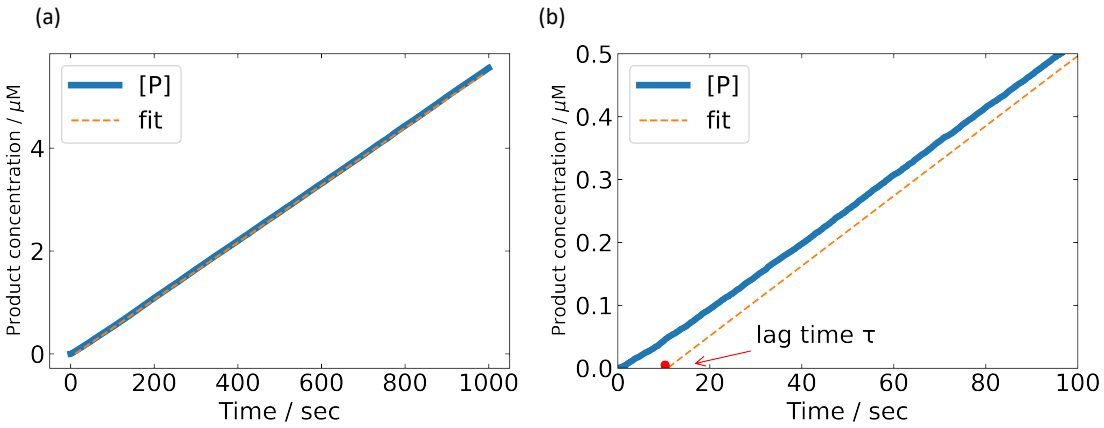

Fig. S5 Product concentration versus time at IS = 120 mM in the KMC model.

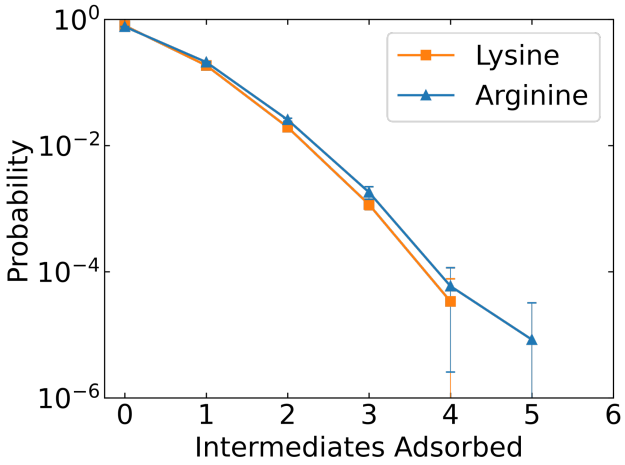

Fig. S6 Probability distribution of the number of adsorbed intermediates on the poly-lysine bridge and poly-arginine bridge.

Table S1. Energy barriers and rate constants

IS mM	G_{hop} kJ/mol	ΔG_{des} kJ/mol	ΔG kJ/mol	$\frac{k_{hop}}{k_{des}}$	$\frac{k_{ads}}{k_{des}} \times 10^6$
0	25.1	47.4	22.3	7515	179
20	25.1	45.6	20.5	3652	87
40	25.1	42.6	17.5	1096	26
70	25.1	41.2	16.1	625	15
120	25.1	36.7	11.6	103	2.5

IS: ionic strength

G_{hop}, k_{hop}: energy barrier and rate constant of hopping on the bridge from one triple association to an adjacent triple association

ΔG_{des}, k_{des}: energy barrier and rate constant of desorption from triple association

ΔG: the energy difference between hopping and desorption $\Delta G = G_{des} - G_{hop}$

Table S2. KMC parameters

Region	Parameter	Value
System	$c_{HK-G6PDH}$, cascade concentration, mol L^{-1}	8×10^{-9}
	Vol, reaction volume, L	2.1×10^{-14}
	c_{sub}, substrate concentration for HK, mol L^{-1}	2
HK	k_{cat}^{HK}, TOF of HK, molec s^{-1}	0.7
	k_{des}^{HK}, desorption rate on HK, s^{-1}	0.07
	k_{ads}^{HK}, absorption rate on HK, s^{-1}	7.7×10^{4}
	k_{hop}^{1b}, hopping rate from HK to bridge, s^{-1}	k_{hop}
	$K_{M,1}^{HK}$, Michaelis constant of HK, mM	10^{-5}
Bridge	k_{hop}, hopping rate on bridge, s^{-1}	$k_{cat}^{HK} \times 100 = 70$
	k_{des}, desorption rate on bridge, s^{-1}	$\frac{k_{hop}}{k_{hop}/k_{des}}$
	k_{ads}, adsorption rate on bridge, s^{-1} mol^{-1} L	$k_{des} \times (k_{hop}/k_{des})$
G6PDH	k_{hop}^{b2}, hopping rate from bridge to G6PDH, s^{-1}	k_{hop}
	k_{cat}^{G6PDH}, TOF of G6PDH, molec s^{-1}	6.2
	k_{des}^{G6PDH}, desorption rate on G6PDH, s^{-1}	0.62
	k_{ads}^{G6PDH}, absorption rate on G6PDH, s^{-1}	1.3×10^{6}
	$K_{M,2}$, Michaelis constant of G6PDH, mM	5.4×10^{-6}

* The value of k_{hop}/k_{des} is from Table S1.