Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supplemental Information

Kinetic Enhancement in High-Activity Enzyme Complexes Attached to Nanoparticles

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Mathematica Model parameters for points or curves in Figure 3

Panel A.

No QD: number of sites=0, k_1=2.3676, k_{-1}=.1, k_2=1.5*10^6, k_{-2}=0, k_3=410, k_{-3}=.01, k_4=k_{-4}=k_5=k_{-5}=0, k_6=k_7=0, k_{-6}=k_{-7}=0

2: number of sites=2, k_1=2.3676, k_{-1}=.1, k_2=1.5*10^6, k_{-2}=0, k_3=410, k_{-3}=.01, k_4=k_{-4}=k_5=k_{-5}=0, k_6=k_7=55760, k_{-6}=k_{-7}=0.01

5: number of sites=5, k_1=2.3676, k_{-1}=.1, k_2=1.5*10^6, k_{-2}=0, k_3=410, k_{-3}=.01, k_4=k_{-4}=k_5=k_{-5}=0, k_6=k_7=22550, k_{-6}=k_{-7}=0.01

Panel B.

Green dashed line: number of sites=500, k_1=2.3676, k_{-1}=.1, k_2=1805.6, k_{-2}=0, k_3=410, k_{-3}=.01, k_4=.165731, k_{-4}=.1, k_5=k_1, k_{-5}=k_{-1}, k_6=5330000, k_7=2050000, k_{-6}=k_{-7}=0.01

Red dashed line: number of sites=1000, k_1=2.3676, k_{-1}=.1, k_2=1805.6, k_{-2}=0, k_3=410, k_{-3}=.01, k_4=.165731, k_{-4}=.1, k_5=k_1, k_{-5}=k_{-1}, k_6=5330000, k_7=2050000, k_{-6}=1.3, k_{-7}=0.01

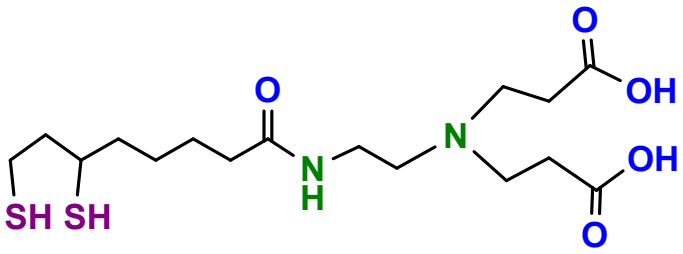

Figure S1. Chemical structure of the compact ligand 4 (CL4) used to cap exchange the QDs and stabilize them in buffer. The molecule is shown in the thioctic acid form. {Susumu, 2011}

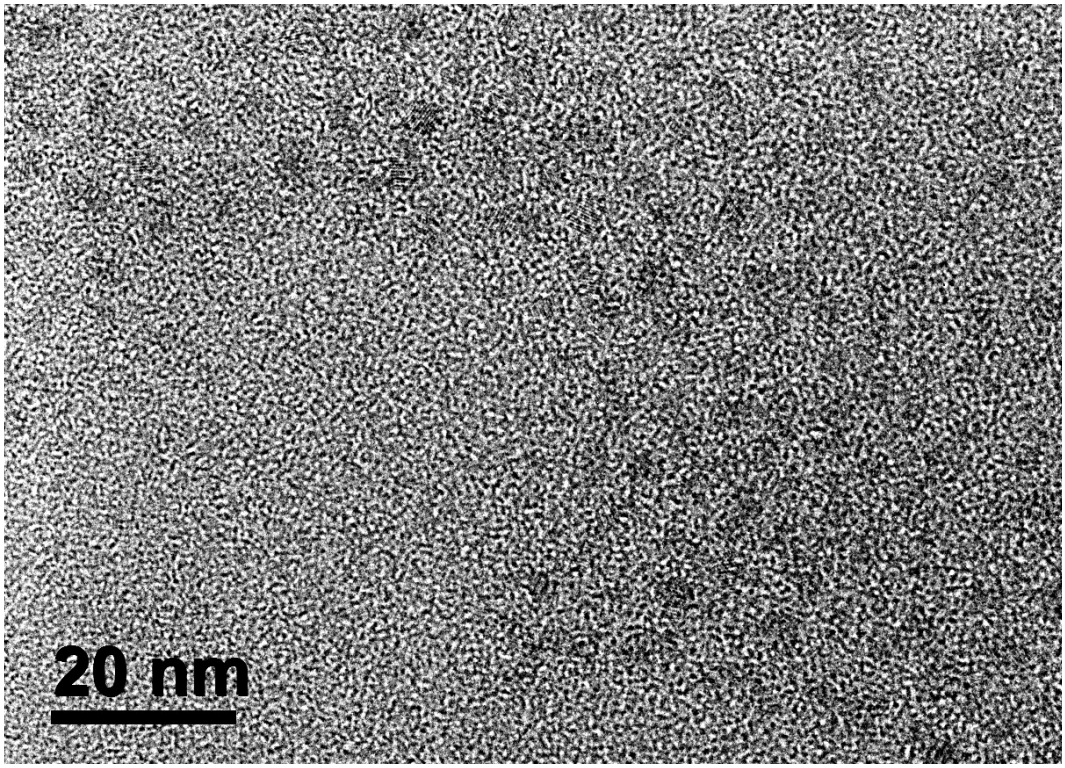

Figure S2. Representative TEM of the 525 nm emitting CdSe/ZnS core/shell QDs utilized in this study. TEMs were collected and analyzed as described in Ref.{Oh, 2013}{Oh, 2016}

Supplemental Table 1. Kinetic parameters for changes in viscosity using Michaelis-Menten form

$QD_{525\ nm}$:β-gal	Glycerol (%)	η_s/η_w	V_{max} (μM s^{-1})	k_{cat} (s^{-1})	K_M (μM)	k_{cat} / K_M (μM^{-1} s^{-1})
0	0.0%	1.0	0.88±0.02	438±11	81±10	5.94
0	4.9%	1.2	1.66±0.05	828±26	894±83	1.02
0	10.5%	1.5	1.89±0.06	945±34	2334±175	0.45
0	18.3%	1.9	1.42±0.08	709±40	2764±313	0.28
0	23.7%	2.0	1.12±0.12	559±63	3431±727	0.18
0	28.3%	2.2	1.22±0.12	608±61	5329±869	0.13
0	34.9%	2.6	0.96±0.14	479±69	5968±1359	0.09
0	40.4%	2.9	0.76±0.08	380±42	8183±1310	0.05
4	0.0%	1.0	2.81±0.11	1416±56	272±45	5.72
4	4.93%	1.2	3.04±0.08	1520±39	950±69	1.76
4	10.5%	1.5	3.01±0.08	1505±40	2014±120	0.82
4	18.3%	1.9	2.20±0.10	1102±52	3084±282	0.39
4	23.7%	2.0	2.44±0.14	1222±73	5817±551	0.23
4	28.3%	2.2	1.66±0.10	828±48	4833±473	0.19
4	34.9%	2.6	1.50±0.14	748±70	7841±1069	0.10
4	40.4%	2.9	0.76±0.07	381±37	6095±925	0.07

Supplemental Table 2. Kinetic parameters for product inhibition using Michaelis-Menten form

$QD_{525\ nm}$:β-gal	Lactose (μM)	V_{max} (μM s^{-1})	k_{cat} (s^{-1})	K_M (μM)	k_{cat} / K_M (μM^{-1} s^{-1})
0	0	0.84±0.04	422±14	97±16	4.34
0	0.01	0.75±0.04	376±17	87±26	4.32
0	0.1	0.83±0.04	415±17	103±21	4.02
0	1	0.90±0.04	454±20	126±27	3.60
0	10	0.80±0.04	404±25	107±33	3.78
0	100	0.54±0.02	272±6	140±16	1.94
0	1000	0.56±0.02	283±11	590±79	0.48
0	10000	0.55±0.04	277±44	3548±1048	0.08
4	0	2.88±0.14	1438±74	290±62	4.96
4	0.01	2.97±0.12	1484±64	263±48	5.64
4	0.1	2.76±0.14	1382±70	284±50	4.86
4	1	2.90±0.14	1449±69	327±62	4.44
4	10	2.53±0.12	1263±60	259±52	4.88
4	100	2.56±0.12	1279±55	227±43	5.62
4	1000	3.30±0.20	1652±103	667±127	2.48
4	10000	2.83±0.54	1414±273	4126±1405	0.34

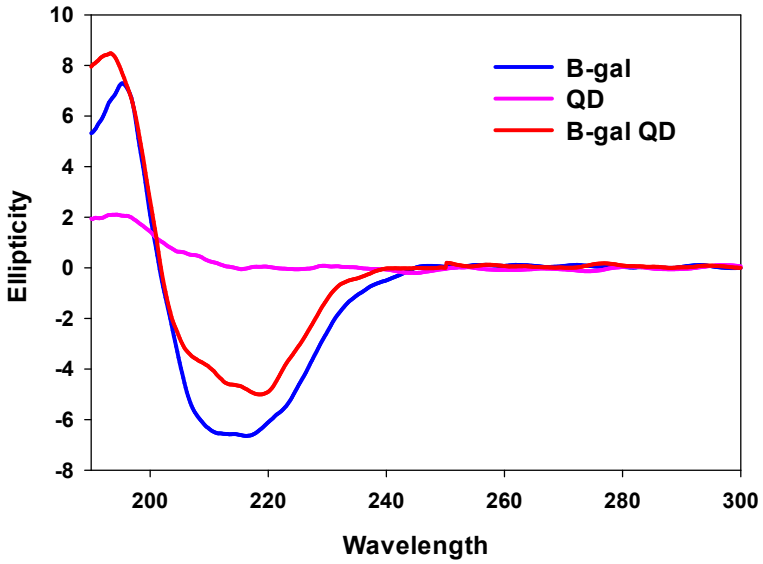

Figure S3. Representative circular dichroism spectra collected from samples consisting of β-gal alone, the 525 QDs alone, and β-gal assembled with QD at a ratio of 4 QD/β-gal. Ellipticity is expressed as the mean residue molar ellipticity (θ) in deg cm^2 dmol^{-1}. Data were collected and analyzed as in ref.{ Boeneman Gemmill, 2015 }

Supplemental References.

1. Susumu, K., Oh, E., Delehanty, J.B., Blanco-Canosa, J.B., Johnson, B., Jain, V., Hervey, W.J., Algar, W.R., Boeneman, K., Dawson, P., Medintz, I.L. Multifunctional compact zwitterionic ligands for preparing robust biocompatible semiconductor quantum dots and gold nanoparticles. *Journal of the American Chemical Society*, 133, 9480–9496 (2011).

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