Electronic Supplementary Information (ESI):

Table S1. The fitted results for the PL decay spectra in Figure 1c.

Sample	y_0	A_1	τ	goodness of fitting
Well modified QDs	1.51	475.8	10.1	0.99
Moderately modified QDs	1.49	478.1	8.0	0.98

*The mono-exponential equation of $y = y_0 + A_1 e^{-x/\tau}$ was used for the fitting. The variables x and y in this equation respectively assign to the decay time and counts in Figure 1c.

Note S1. The calculation of ligand density outside ODs.

The volume of one CdTe QD (V_{CdTe}) can be calculated via spherical volume equation:

$$V_{CdTe} = \frac{4}{3}\pi(R_{CdTe})^3 \qquad (1)$$

where R_{CdTe} is radius of one CdTe QD. Since the average size of CdTe QDs is 2.4nm calculating from the excitonic peak position in Figure 1a, R_{CdTe} is 1.2nm in this work.

The amount of substance of CdTe in one QD (n_{CdTe}) can be expressed as:

$$n_{CdTe} = \frac{\rho_{CdTe} V_{CdTe}}{M_{CdTe}} \qquad (2)$$

where ρ_{CdTe} is the density of zinc blend CdTe crystals. The value is 5.85 g/cm^3. M_{CdTe} is molecular weight of CdTe with a value of 240g/mol.

In case of 1 monolayer of Cd-TG ligand shell outside CdTe QD, the volume of ligand shell (V_{CdS}) can be calculated by the difference between spherical volume with and without ligand shell:

$$V_{CdS} = \frac{4}{3}\pi(R_{CdTe} + R_{CdS})^3 - \frac{4}{3}\pi(R_{CdTe})^3 \qquad (3)$$

where R_{CdS} is the thickness of one monolayer of Cd-TG ligand shell. To simplify the calculation, we used the thickness of one monolayer of CdS (0.35nm) in this work.

The amount of substance of CdS in one QD (n_{CdS}) can be expressed as:

$$n_{CdS} = \frac{\rho_{CdS}V_{CdS}}{M_{CdS}} \qquad (4)$$

where the density of CdS (ρ_{CdS}) is 4.82 g/cm³.

The atomic ratio of S/Te can be calculated by n_{CdS}/ n_{CdTe} according to the results of equation (4) and (2). The calculated S/Te atomic ratio is 1.58 for 1 monolayer ligand shell outside 2.4nm CdTe QDs. According to the measured S/Te ratios in XPS in Figure 2, the ligand density outside CdTe QDs are 0.97 monolayer for well modified QDs and 0.61 monolayer for moderately modified QDs respectively.

Note S2. Deduction of expression of discriminative detection of Mn(II) in a target sample in simultaneous presence of Mn(II) and Cu(II).

The prerequisite 1 for discriminative detection of Mn(II) is the unchanged prepserved PL ratio Cu(II) detection at different pH, which can expressed by:

PR 8.2$_{Cu}$- PR X$_{Cu}$=0   (X>8.2)   (1)

where 8.2 and X indicate pH of QD buffer solution. The subscript Cu implys the type of sensitive cation in the solution.

The prerequisite 2 for discriminative detection of Mn(II) is the preserved PL ratio is 100% at pH 8.2 during Mn(II) detection, thus the following equation should be expressed:

PR 8.2$_{Mn}$- PR X$_{Mn}$=1-PR X$_{Mn}$ (X>8.2)   (2)

The prerequisite 3 for discriminative detection of Mn(II) is no ionic couple effect to QDs when the target sample containing both Mn(II) and Cu(II). The effect of the mixture of Mn(II) and Cu(II) can be simply seen as the effect of Mn(II) plus the effect

of Cu(II) as expressed as:

$$\text{PR } 8.2_{Mn+Cu} = \text{PR } 8.2_{Mn} + \text{PR } 8.2_{Cu} \qquad (3)$$

$$\text{PR } X_{Mn+Cu} = \text{PR } X_{Mn} + \text{PR } X_{Cu} \qquad (X>8.2) \qquad (4)$$

According to three prerequisites, the discriminative detection of Mn(II) can be expressed as:

$$\text{PR } 8.2_{Mn+Cu} - \text{PR}X_{Mn+Cu} = (\text{PR } 8.2_{Mn} + \text{PR } 8.2_{Cu}) - (\text{PR } X_{Mn} + \text{PR } X_{Cu})$$

$$= (\text{PR } 8.2_{Mn} - \text{PR } X_{Mn}) + (\text{PR } 8.2_{Cu} - \text{PR } X_{Cu})$$

$$= 1 - \text{PR } X_{Mn} \qquad (5)$$

or expressed as:

$$1 - \text{PR } 8.2_{Mn+Cu} + \text{PR } X_{Mn+Cu} = \text{PR } X_{Mn} \qquad (X>8.2) \qquad (6)$$

In this expression, PR 8.2_{Mn+Cu} and PR X_{Mn+Cu} are measured by the target sample containing both Mn(II) and Cu(II) at two different pH. PR X_{Mn} is measured by a standard sample with sole presence of Mn(II). This standard sample can be known from Figure 4 in the text. According to equation 6, when the target sample containing both Mn(II) and Cu(II), the concentration of Mn(II) can be recognized by comparising the preserved PL ratios at two different pH (namely 1 - PR 8.2_{Mn+Cu} + PR X_{Mn+Cu}) with a standard sample at pH X (namely PR X_{Mn}) with containing only Mn(II).