Electronic Supplementary information (ESI) for Nanoscale:

Bright Type-II Photoluminescence from Mn-Doped CdS/ZnSe/ZnS Quantum Dots with Mn²⁺ Ions as Exciton Couplers

Ruilin Xu,^a Chen Liao,^a Yanqing Xu,^b Chunfeng Zhang,^{*b} Min Xiao,^b Lei Zhang,^a Changgui Lu,^a Yiping Cui,^a and Jiayu Zhang^{*a}

^aAdvanced Photonic Center, Southeast University, Nanjing 210096, China

^bNational Laboratory of Solid State Microstructures, School of Physics, Nanjing University,

Nanjing 210093, China

Corresponding Author

*E-mail: jyzhang@seu.edu.cn.

*E-mail: cfzhang@nju.edu.cn.



Fig. S1 Evolution of the confinement of core/shell CdS/ZnSe quantum dots (QDs) with shell thickness. (a) CdS/ZnSe QDs with thin shell correspond to the quasi type-II regime, in which the electron is localized in the core but the hole is delocalized over the entire QD volume. (b) CdS/ZnSe QDs with thick shell correspond to the true type-II regime, in which the electron and hole are separated between the core and the shell.¹

Element	Cd	Mn	Zn
Concentration (mg/L)	26.2	0.239	2.34
Molar ratio	1	0.019	0.154
Molar percentage (<mark>X</mark> /(Cd+Mn+Zn))	85.3%	1.6%	13.1%

Table S1 The compositions of the Mn-doped cores measured by means of inductively coupled plasma optical emission spectroscopy. The sample was prepared by dissolving the QD powder in HCl/HNO₃.



Fig. S2 (a) PL spectra of Mn-doped seed cores at different excitation wavelengths. (b) The Mn-doped cores with a designed structure of MnS/ZnS/CdS. (c) The schematic diagram of PL processes at different excitation wavelengths in the naked core with a large spatial heterogeneity.

As shown in Fig. S2(a-c), due to the designed spatial heterogeneity (Fig. S2(b)), an excitation light with a shorter wavelength excites the inner layers of QDs, which decreases the exciton trapping rate by surface traps but increases the exciton- Mn^{2+} energy transfer rate, leading to less surface state emission but more Mn^{2+} emission (Fig. S2(c)). The strong spatial heterogeneity of cores provides a good opportunity of reflecting the sites of Mn^{2+} dopants by the PL spectra at

different excitation wavelengths, which provided a strong direct proof of the fact that the cores were inner-doped with Mn²⁺ ions. We did not observe the similar change in PL spectra with excitation wavelengths in the CdS/ZnSe/ZnS or CdS/ZnS QDs with the same cores, because the shell capping and the thermal annealing remove the naked CdS cores' surface traps and the thermal annealing enhances the uniformity of cores.

In conclude, the seed cores were inner-doped with Mn^{2+} ions, and the molar ratio of Mn/Cd is 0.019. Additionally, the sites of luminescent centers (such as Mn^{2+} ions) can also be verified by the PL spectra obtained by changing the excitation wavelengths.



Fig. S3 PL spectra of Mn-doped CdS/ZnS and CdS/ZnSe/ZnS QDs respectively. Both Mn-doped CdS/ZnS and CdS/ZnSe/ZnS QDs possess the same inner-Mn-doped cores prepared by the nucleation-doping strategy; and their giant shells were prepared by the similar processes of optimized "flash" synthesis. In Mn-doped QDs, the energy difference between exciton and Mn^{2+} ${}^{4}T_{1}$ (ΔE) acts as the thermodynamic driving force for net energy transfer (ET). A large ΔE will lead to a large net ET and a dominant Mn^{2+} emission. A small ΔE will lead to a strong bidirectional coupling between exciton and Mn^{2+} ${}^{4}T_{1}$ but nearly no Mn^{2+} emission due to spin-forbidden. The general law of PL dynamics in Mn-doped QDs is vividly shown in Fig. S10.



Fig. S4 Stable photoluminescence (PL) spectra of undoped and Mn-doped CdS/ZnSe/ZnS QDs. Dot curves were obtained by single-peak Gaussian fitting. For the undoped QDs, the fit curves of both stable PL spectra and integrated (within 500 ns) PL spectra match well with the corresponding PL spectra. While for the Mn-doped QDs, the difference between the integrated (within 500 ns) PL spectra and the corresponding fit curve is slightly larger than the difference between the stable PL spectra and the corresponding fit curve, which may be attributed to the longer PL lifetime of Mn-doped QDs than that of undoped QDs.

Undoped CdS/ZnSe/ZnS QDs		Mn-doped CdS/ZnSe/ZnS QDs		
A ₁	0.379	A ₁	0.388	
τ1	11.2 ns	τ_1	12.8 ns	
A ₂	0.455	A ₂	0.406	
τ_2	38.7 ns	τ_2	44.4 ns	
A ₃	0.126	A ₃	0.182	
τ3	195.3 ns	τ ₃	324.7 ns	

Table S2 Multi-exponential fitting parameters of PL decays of undoped and Mn-dopedCdS/ZnSe/ZnS QDs at PL peak (~550 nm).

The averaged PL lifetimes (τ_{aver} , 119 ns and 244 ns respectively) were calculated using the formula of $\tau_{aver} = (A_1 \tau_1^2 + A_2 \tau_1^2 + A_3 \tau_1^2)/(A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3)$.² For the QDs with ZnS shell of ~2 MLs, the increased ratio of PL lifetime is calculated as 2.05. While the PL quantum yield (QY) enhancement factor is 1.70 (from 37% to 63%); accordingly the radiative rate of excitons is just decreased to 0.83 according to the formula of PLQY = $\frac{k_R}{k_R + k_{NR}} = k_R \tau_{aver}$ (k_R and k_{NR} represent radiative and nonradiative rates respectively).³ The slightly-changed radiative rate of the Mn-doped QDs is attributed to the rapid population exchange between exciton and $Mn^{2+4}T_1$ established by the rapid bidirectional ET. The energetically-favorable forward ET is rapid, while the thermally-activated back ET is also rapid at room temperature, resulting from a small energy difference between two excited states with a strong coupling (more details in Fig. S7). Accordingly, the increased PL lifetime of the Mn-doped QDs is mainly attributed to the decreased nonradiative rate by the strong exciton-Mn²⁺ coupling.



Fig. S5 Evolutions of $-\Delta OD$ of $1S_{CdS}$ and $1S_{CdS-ZnSe}$ within 100 ps.



Fig. S6 Contour plots of the experimental TA spectra of undoped (a) and Mn-doped (b) CdS/ZnSe/ZnS QDs (λ pump = 350 nm) at early stage within 10 ps.

CT Abs-peak (~505 nm)								
Undoped			Mn-doped					
A_1	0.101	τ_{fast}	A_1	0.252	τ_{fast}	$ au_{ m ET}$		
τ_1	16.0 ps	Tubt	τ_1	15.7 ps	Tust			
A ₂	0.341	168 ps	A ₂	0.427	96 ps	224 ps		
τ_2	212.8 ps	-	τ_2	143.3 ps	-	-		
A ₃	0.516		A ₃	0.322				
τ_3	3.68 ns		τ_3	2.77 ns				

Table S3 Multi-exponential fitting parameters of –ΔOD probed at CT Abs-peak (~505 nm) of

these undoped and Mn-doped QDs.



Fig. S7 Strongly coupled system of exciton and $Mn^{2+4}T_1$ with rapid population exchange.

According to W.Y. Liu and V. I. Klimov,⁴ the relationship between populations of exciton (N_{exc}) and $\text{Mn}^{2+4}\text{T}_1(N_{\text{Mn}^*})$ can be expressed as

$$N_{\rm exc} = N_{{\rm Mn}^*} e^{-\alpha \Delta E/kT}$$

which shows a special statistics on the population of higher-energy excited states in a coupled system, differing from the classical Boltzmann statistics. Probably, the superposition principle of quantum mechanics plays an important role in the statistics on the population of higher-energy excited states in a coupled system with rapid population exchange. A Schrodinger cat lives in the strongly coupled system, which leads to the divergence and unclarity. We firstly put forward the hypothesis during the study of radiative rate of the strongly coupled system. Taking one example to make it more acceptable, one exciton is generated in a Mn-doped QD with the bidirectional ET between exciton and $Mn^{2+4}T_1$ ($E_{exc}>E_{Mn^*}$): for the Mn^{2+} emission, the population of $Mn^{2+4}T_1$ is 1; while for the exciton emission, the population of exciton is also 1 as long as the back ET is still much faster than the exciton recombination ($k_{BET} \ge \sim 10k_{exc}$). Further, the population statistics of "strongly coupled" excited states needs to be studied thoroughly and systematically. Based on the above formula of population, we can get the formula of radiative rate of the system ($E_{exc} > E_{Mn^*}$), as follows:

$$k_{\text{R_system}} = k_{\text{R_exc}} e^{-\alpha \Delta E/kT} + k_{\text{R_Mn}}.$$

The contribution to the radiative rate of system from Mn^{2+} ions is k_{R_Mn} , which can be ignored in this study ($k_{R_Mn} \ll k_{R_system}$). So there is nearly no Mn^{2+} emission, but Mn^{2+} ions play an important role. The opposite dynamical shiftings in transient spectra and the shift in stable PL spectrum are attributed to the strong coupling from Mn^{2+} ions. Further, we can get the simplified formula as follows:

$$k_{\rm R_system} \approx k_{\rm R_exc} e^{-\alpha \Delta E/kT}$$

The decrease in population of higher-energy states is suppressed by " α <1", which probably results from the strong coupling; and then the decrease in radiative rate is suppressed. According to the formula, the radiative rate of the strongly coupled system can be nearly unchanged under the condition of a small energy difference (ΔE) between exciton and excited dopant ions. Notably, the radiative rate of the excion (k_{R_exc}) is not changed by the coupling from Mn²⁺ ions; while, the radiative rate of the strongly coupled system (k_{R_exc}) is just decreased by the decreasing population of the exciton.



Fig. S8 Kinetic models for the analysis of PLQY increased by Mn^{2+} ions.

After the introduction of Mn^{2+} ions into these type-II QDs, the PLQYs were increased significantly. For these CdS/ZnSe QDs, the increased ratio of PLQY could be greater than 3 (from $\leq 5\%$ to $\sim 15\%$). For these QDs with ZnS shell of ~ 2 MLs and ~ 5 MLs respectively, the increased ratio of PLQY was 1.7 (from 37% to 63%) and 1.9 (from 26% to 50%) respectively.

Immediately after photoexcitation, type-I excitons were generated and after ultrafast charge transfer (CT) the CT excitons fastly relaxed into hot CT excitons via carrier thermalization process^{5,6} (~1 ps) due to excess energy. Subsequently, the hot CT excitons cooled via exciton-phonon (~100 ps) and phonon-phonon coupling (~1–100 ns) processes.^{5,6} Exciton could recombine radiatively during exciton cooling, but the time of main cooling process (within ~100 ps) is much shorter than the long recombination lifetime of excitons (~100 ns). Thus, in the kinetic model, the slowest cold-exciton recombination at PL bandgap is regarded as the final step. Accordingly, the PLQY is simply expressed as PLQY = $\Phi_{\text{Relax}-1}\Phi_{\text{Relax}-2}\Phi_{\text{PLBG}}$, where $\Phi_{\text{Relax}-1}$ and $\Phi_{\text{Relax}-2}$ denote the relaxation efficiency from type-I excitons to CT excitons and

from hot CT excitons to cold CT excitons respectively, and Φ_{PLBG} denotes the final radiative recombination efficiency at PL bandgap (PLBG). For the PLQY of these Mn-doped QDs, we have the formulas as follows: $\Phi_{Relax-2} = \frac{k_{Cooling-2}+k_{ET}}{k_{Cooling-2}+k_{ET}+k_{Trapping}}$ (for a single QD), $\Phi_{Relax-2} = \frac{k_{Cooling-2}+k_{ET}}{k_{Cooling-2}+k_{ET}+k_{Trapping}}$

$$1 - \frac{k_{\text{Trapping}}}{k_{\text{Trapping}} + k_{\text{Cooling}} + k_{\text{ET}}} A_{\text{Fast}} \text{ (for the QD ensemble).}$$

It is hard to calculate the absolute PLQY using such formula, but by analyzing the combination of TA and TP (or the corresponding PLQY) it is probable to compare the efficiency ratio between the similar processes of the similar systems. Mn²⁺ ions as exciton couplers enhance the PLQY by the strong coupling of rapid ET (coupling-1) and the strong bidirectional coupling (coupling-2). The PL enhancement factor due to coupling-1 (PEF1) can be estimated by analysis of TA. While the PL enhancement factor due to coupling-2 (PEF2) cannot be measured separately, but can be deduced by the combination of TA and TP (or the corresponding PLQY). That is because the PL decay can also be slowed by back feeding extra energy to exciton states (a shift in thermal equilibrium), besides by reducing nonradiative transition by the strong bidirectional coupling.

A multi-exponential decay over a wide time frame (~1.8 ns) may be convoluted with carrier cooling, the slow component of charge transfer, the defect trapping, and exciton recombination.^{4,5} Accordingly, now we try to estimate the enhanced ratio of the latter two items, i.e. $\Phi_{\text{Relax-2}}$ and Φ_{PLBG} . For the estimation of increased ratio of $\Phi_{\text{Relax-2}}$ (Fig. 4a, in main body of this article), the k_{ET} is 1/224 ps⁻¹, and the k_{Total} is 1/168 ps⁻¹ and 1/96 ps⁻¹ carrying 50% and 70% of the amplitude for undoped and Mn-doped QDs respectively. If k_{Total} 1/168 ps⁻¹ of undoped QDs is all assigned to the exciton-trapping (i.e. slow cooling with $k_{\text{Cooling}} \ll 1/168 \text{ ps}^{-1}$; that corresponds to a slow cooling time of hot charge-transfer excitons in the timescale of ns)⁷, the

ratio of $k_{\rm ET}$ and $k_{\rm Trapping}$ is 0.75, so $\frac{k_{\rm Trapping}}{k_{\rm Trapping} + k_{\rm ET}}$ equals 0.57 carrying about 70%. Accordingly, the ratio of trapped excitons is reduced from the 50% to 40% (=70%*0.57), which means the ratio of effective excitons is increased from the 50% to 60%. Thus, the enhancement factor of $\Phi_{\rm Relax-2}$ is estimated as 1.2 by analyzing at type-II Abs peak of ~505 nm.

To sum up, for the undoped and Mn-doped CdS/ZnSe/ZnS QDs with ZnS shell of ~5 MLs, the enhancement factor of $\Phi_{\text{Relax-2}}$ due to "ETSs" is estimated to be 1.2. While the enhancement factor of PLQY is 1.9 (from 26% to 50%). Accordingly, the enhancement factor of Φ_{PLBG} due to "couplers" is estimated to be 1.6. The estimation is simplified, but anyhow it verifies that exciton trapping could be decreased by competitions between Mn²⁺ ions and traps in both two stages of rapid ET and thermal equilibrium.

In a word, Mn^{2+} ions act as ETSs of hot excitons (coupling-1) and couplers of cold excitons (coupling-2) to enhance CT exciton emission.



Fig. S9 The PL enhancement factor due to the continuous competition between Mn^{2+} ions and traps.

In mathematics, the enhancement factor of successive events equals to the product of a serial of enhancement factors corresponding to continuous enhancement events. Fig. S9 shows a typical example of PL enhancement. For the QDs with ZnS shell of ~5 monolayers (MLs), the increased ratio of photoluminescence (PL) quantum yield (QY) was 1.9 (from 26% to 50%) due to Mn^{2+} doping; during rapid ET, the enhancement factor is 1.2, while during long thermal equilibrium, the enhancement factor is 1.6. In conclude, the competition between Mn^{2+} ions and traps continuously proceeds in both processes of rapid ET and long thermal equilibrium with strong coupling between exciton and $Mn^{2+} {}^{4}T_{1}$; and the PEF of these two processes equals to the product of PEF1 and PEF2.



Fig. S10 The general law of PL dynamics in Mn-doped QDs. The PL dynamics changes with the energy difference between exciton and $Mn^{2+4}T_1(\Delta E)$ as the thermodynamic driving force.

|Exciton> represents the exciton state of Mn-doped QDs, while |Mn*> represents the Mn^{2+ 4}T₁ as the lowest excited state of Mn²⁺ ions. Δ*E* represents the energy difference between exciton and Mn^{2+ 4}T₁. N_{exc} and N_{Mn^*} represent the populations of exciton and Mn^{2+ 4}T₁ respectively. N_{total} represents the total population of exciton and Mn^{2+ 4}T₁. In this QDs ($E_{exc}>E_{Mn^*}$) with rapid population exchange between exciton and Mn^{2+ 4}T₁, N_{total} is equal to N_{Mn^*} . k_{ET} represents the forward ET rate, while k_{BET} represents the back ET rate; they are QD-system-specific constants, and k_{BET} (= $k_{ET}e^{-\alpha\Delta E/kT}$) decreases with the increasing ΔE . k_{ET-Net} (= $k_{ET} - \frac{N_{Mn^*}}{N_{exc}}k_{BET}$) represents the net ET rate of the QD ensemble, which decreases continuously with the decreasing N_{exc} before thermal equilibrium and changes from k_{ET} to about 0. It changes with population evolution of two excited states, which shows the statistical significance. To differentiate with the expressions of forward ET and back ET, the expression of ET without modifiers usually depicts the net ET. PEF1 represents the PL enhancement factor due to the ET, while PEF2 represents the PL enhancement factor due to the coupling during thermal equilibrium.

The smaller ΔE , the larger k_{BET} , the smaller $k_{\text{ET-Net}}$, and the smaller PEF1, but the larger coupling between exciton and Mn^{2+ 4}T₁, and then the larger PEF2. Conversely, the larger ΔE , the smaller k_{BET} , the larger $k_{\text{ET-Net}}$, and the larger PEF1, but the smaller coupling between exciton and Mn^{2+ 4}T₁, and then the smaller PEF2. Notably, an ultra-large ΔE can result in that the back ET rate (k_{BET}) is much slower than the total de-excitation rate of Mn²⁺ ions (k_{Mn}), which lead to that the back ET does almost not happen. In this situation of ultra-large ΔE , there is no population exchange between exciton state and Mn^{2+ 4}T₁ after this rapidest ET, which means that the enhancement factor is attributed to the rapid ET; accordingly, the PEF2 is just 1, while the PEF1 reaches the maximum.

For Mn-doped QDs with exciton emission of ~450 nm, the large ΔE between exciton and $Mn^{2+4}T_1$ leads to a large net ET but a small coupling during thermal equilibrium; the rapid ET will enhance the QDs' PL by decreasing both exciton trapping and exciton emission, and this type of QDs can show an intriguing Mn^{2+} emission. While for Mn-doped QDs with exciton emission of ~550 nm, the small ΔE between exciton and $Mn^{2+4}T_1$ leads to a small net ET but a strong bidirectional coupling during thermal equilibrium; the continuous coupling will enhance the QDs' PL by decreasing exciton trapping and this type of QDs can show an intriguing during thermal equilibrium; the continuous coupling will enhance the QDs' PL by decreasing exciton trapping and this type of QDs can show an intriguing exciton emission.

Notably, the coupler with a higher PLQY can be introduced to enhance the PL from the emitter with a lower QY. The PLQY of Mn^{2+} emission is related to the concentration and sites of Mn^{2+} ions.^{8,9} While, the high-concentration or the surface Mn^{2+} ions usually act as the quencher

for both band-edge and Mn^{2+} emission. With the increasing doping concentration, the rate of ET from exciton to Mn^{2+} ions is increased, which will lead to a faster bleach recovery and a faster peak red-shifting at charge-transfer state in TA spectra. In these bright Mn-doped CdS/ZnSe/ZnS QDs (PL peak: ~550 nm), there is nearly no Mn²⁺ emission, which means most of the energy transferred to Mn²⁺ ions feeds back to the exciton states at this applicable doping. When the doping concentration is too high, the exciton emission will be quenched. There will be more energy which is faster transferred from exciton to Mn^{2+} ions, but there will be less energy which is transferred back to exciton states. The exciton trapping by other defects is suppressed but the additional nonradiative transition is introduced and the most of the energy transferred to Mn^{2+} ions can not feed back to the exciton states. Obviously, the PL decay in TP spectra will not be slowed down but be accelerated. Accordingly, inner Mn²⁺ ions with certain concentration favor the acquisition of high PLQY. For type-I QDs, their high intrinsic radiative recombination rate favors a high PLQY, so Mn²⁺ ions can not be introduced to enhance their PLQY obviously. While for type-II QDs, their low intrinsic radiative recombination rate does not favor a high PLQY, so Mn^{2+} ions can be introduced as exciton couplers to enhance their PLQY obviously. The low QY of type-II PL is attributed to both the slow cooling of hot excitons and the low radiative rate of cold excitons. Fortunately, the problems can be solved by the above-mentioned two couplings between exciton and Mn^{2+} excited states respectively. On the one hand, Mn^{2+} ions as the couplers of hot excitons promote the cooling of hot excitons by the ET from hotter excitons to Mn²⁺ ions, instead of promoting the hot electron generation in the condition of multiexciton generation¹⁰⁻¹². On the other hand, Mn^{2+} ions as the couplers of cold excitons further suppress the exciton trapping by the strong bidirectional coupling.

This work provides a unique way of acquiring high QY of type-II PL, lights up the general law of PL enhancement in Mn-doped QDs and even touches the population statistics of "strongly coupled" excited states, which will arouse researchers' wide attention and deeper study.

REFERENCES

- S. A. Ivanov, A. Piryatinski, J. Nanda, S. Tretiak, K. R. Zavadil, W. O. Wallace, D. Werder and V. I. Klimov, J. Am. Chem. Soc., 2007, 129, 11708–11719.
- (2) H.-Y. Chen, S. Maiti and D. H. Son, ACS Nano, 2012, 6, 583–591.
- (3) C. Pu, H. Qin, Y. Gao, J. Zhou, P. Wang and X. Peng, J. Am. Chem. Soc. 2017, 139, 3302–3311.
- (4) W. Liu, Q. Lin, H. Li, K. Wu, I. Robel, J. M. Pietryga, V. I. Klimov, J. Am. Chem. Soc., 2016, 138, 14954–14961.
- (5) C.-H. Chuang and C. Burda, J. Phys. Chem. Lett., 2012, 3, 1921–1927.
- (6) C.-H. Chuang, X. Chen and C. Burda, Ann. Phys., 2013, 525, 43–48.
- (7) A. Pandey and P. Guyot-Sionnest, *Science*, 2008, **322**, 929–932.
- (8) T. J. Norman, D. Magana, T. Wilson, C. Burns, J. Z. Zhang, D. Cao and F. Bridges, J. Phys. Chem. B, 2003, 107, 6309–6317.
- (9) P. H. Borse, D. Srinivas, R. F. Shinde, S. K. Date, W. Vogel and S. K. Kulkarni, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **60**, 8659–8664.

- (10) H.-Y. Chen, T.-Y. Chen, E. Berdugo, Y. Park, K. Lovering and D. H. Son, *J. Phys. Chem. C* 2011, **115**, 11407–11412.
- (11) C. J. Barrows, J. D. Rinehart, H. Nagaoka, D. W. deQuilettes, M. Salvador, J. I. L. Chen, D. S. Ginger and D. R. Gamelin, *J. Phys. Chem. Lett.*, 2017, 8, 126–130.
- (12) Y. Dong, J. Choi, H. K. Jeong and D. H. Son, J. Am. Chem. Soc., 2015, 137, 5549-5554.