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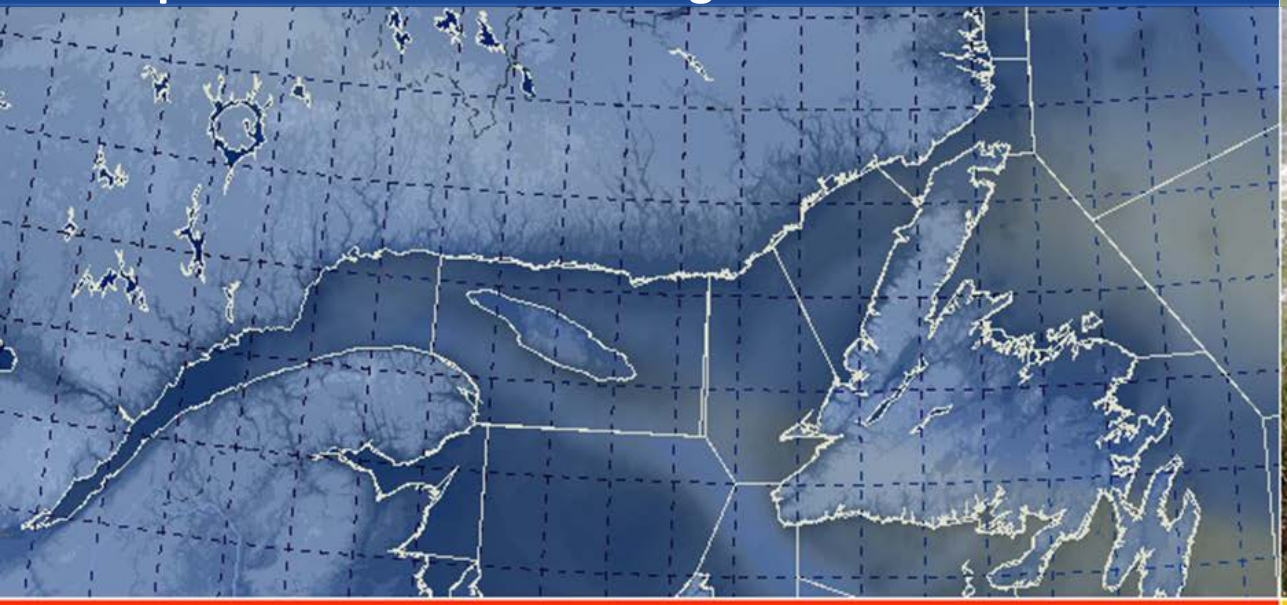
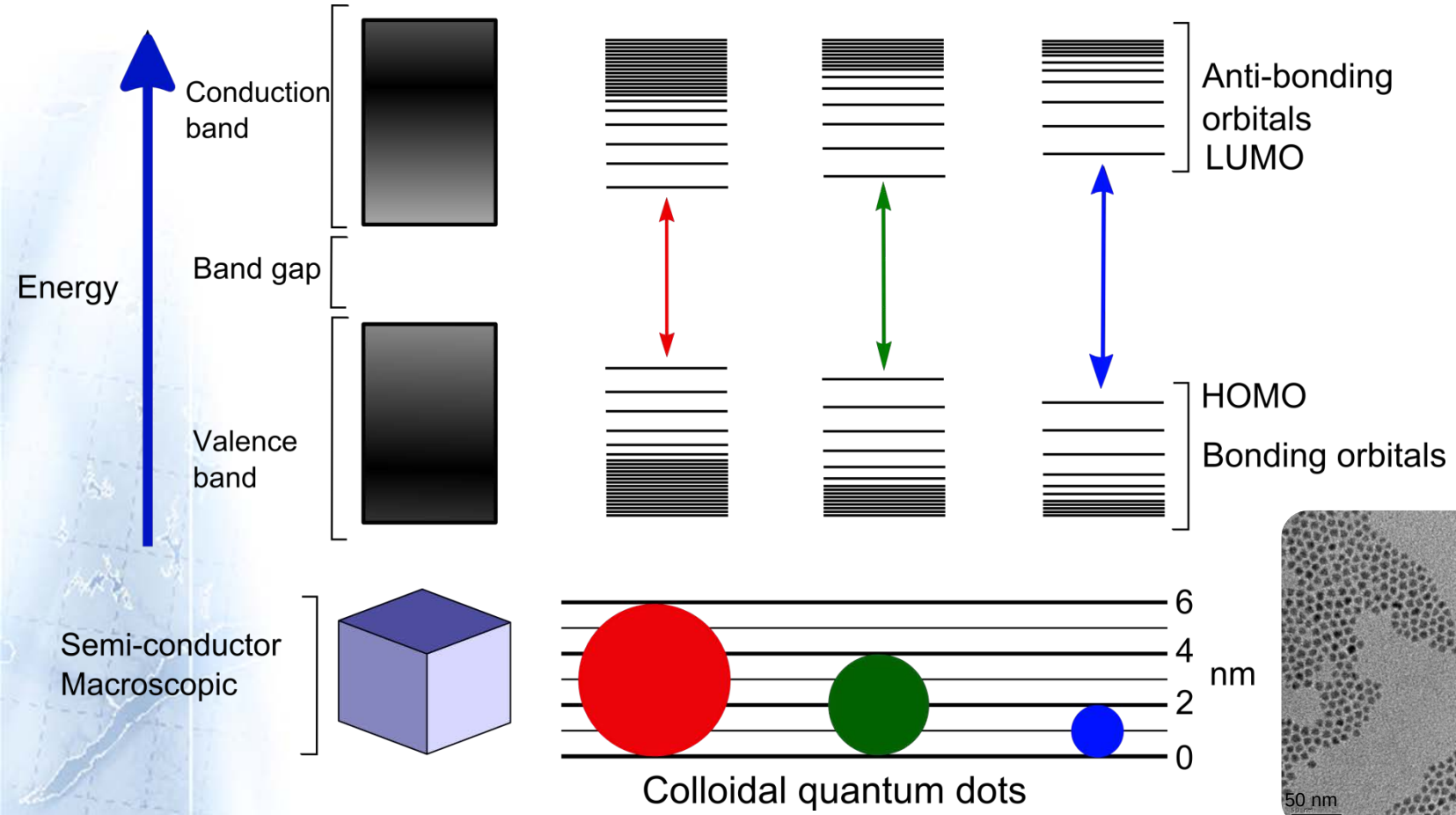
Colloidal quantum dots for applications in dosimetry and liquid scintillation counting



October 27, 2014

COPL Centre d'optique, photonique et laser
Centre de recherche sur le cancer
CHU de Québec
Université Laval, Département de chimie

What are colloidal quantum dots?



Nanocrystals

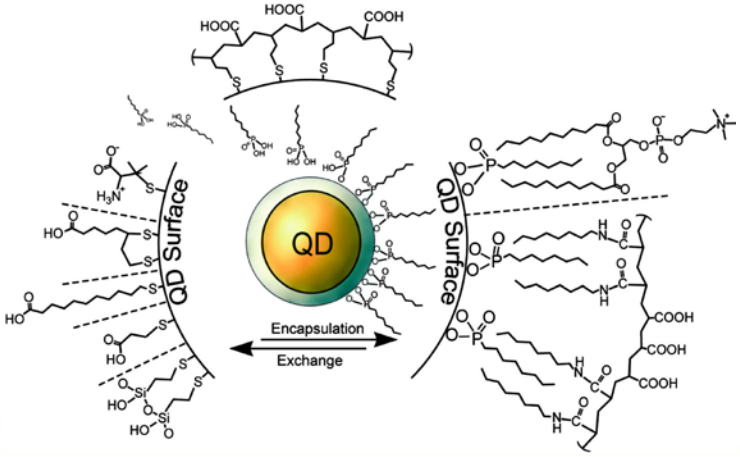
In 1982, Louis E. Brus was the first to discover the properties of CdS nanocrystals. He named them colloidal quantum dots

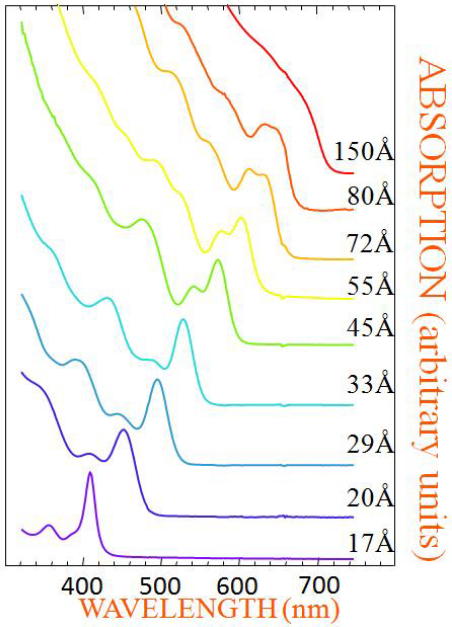
Application	**Colloidal quantum dots**
Electronic devices	PbS, PbSe, CdSe, CdS, ZnSe
Bioimaging	CdSe, CdS, ZnS, CdTe, InP, ZnO
Photovoltaic devices	PbS, PbSe, Graphene
Light-emitting devices	ZnO, CdSe, CdZnSe
Photodetection devices	PbS, PbSe, CdSe, ZnSe, CdS, ZnS

Rossetti, R.; Brus, E. L. *J. Phys. Chem.* **1982**, *86*, 4470.

Properties of semi-conductor nanocrystals

- Tunable emission wavelength
- Large absorption band
- Surface can be functionalized
- High electronic density
- Can be water soluble





http://nanocluster.mit.edu/research.php

Tyrakowski C.M. and Snee P.T., *Phys.Chem.Chem.Phys.*, **2014**, 16, 837.

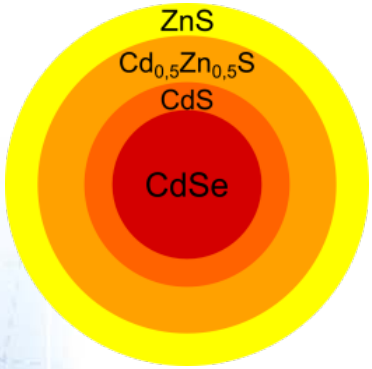
Use in radiation detection

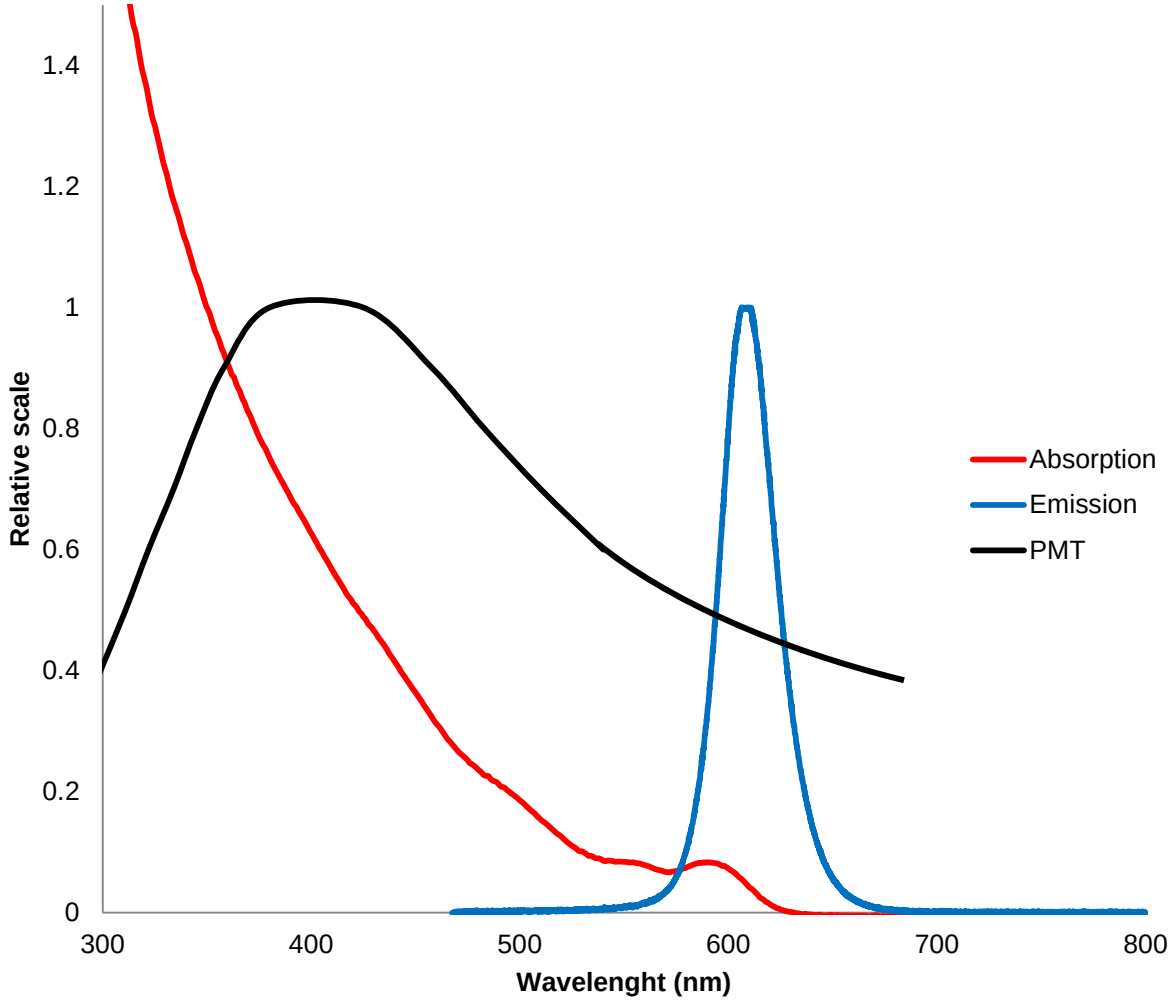
Type of scintillator support	QD system used	Dispersion matrix	Emission wavelenght (nm)	Exposed radiation type	Reference
Glass	CdSe/ZnS	Porous glass	540	α	1
	CdSe/ZnS	Porous glass	510	γ, α	2
	ZnS	Lithiated gel	380	?	3
	CdSe/ZnS	Lithiated gel	590	α	3
Polymer	CdSe/ZnS	Polystyrene	520	γ, α, X-ray	4
	CdSe/ZnS	Polystyrene	472	γ, α	5
	CdTe	PMMA	547	γ	6
	CdSe-ZnSe	MEH-PPV	550	β (3 keV)	7
Liquid	CdSe/CdS/CdZnS/ZnS	Hexane/water	605	γ, α	8
	CdSe/ZnS	Hexane	524	γ	9
	CdS + PPO	Toluene	360 - 420	β	10
	CdSe/ZnS	Hexane	579	γ	11

1) Létant, S.E. and T.-F. Wang, *Applied Physics Letters*, 2006. **88**(10) 103110. 2) Létant, S.E. and T.F. Wang, *Nano Letters*, 2006. **6**(12): 2877. 3) Dai, S., et al., *AIP Conference Proceedings*, 2002. **632**(1): 220 4) Park, J.M., et al., *Journal of Luminescence*, 2014. **146**(0): 157. 5) Brown, S.S., A.J. Rondinone, and S. Dai. *Applications of Nanoparticles in Scintillation Detectors*. in *ACS symposium series*. 2007. Oxford University Press. 6) Wagner, B.K., et al. *Nanocomposites for radiation sensing*. 2012. 7) Campbell, I.H. and B.K. Crone, *Advanced Materials*, 2006. **18**(1): 77. 8) Lecavalier, M.E., et al., *Chemical Communications*, 2013. **49**(99): 11629. 9) Stodilka, R.Z., et al., *The Journal of Physical Chemistry C*, 2009. **113**(6): 2580. 10) Winslow, L. and R. Simpson, *Journal of Instrumentation*, 2012. **7**(07): p. P07010. 11) Withers,. *Applied Physics Letters*, 2008. **93**(17): 173101.

Colloidal quantum dots – initial approach

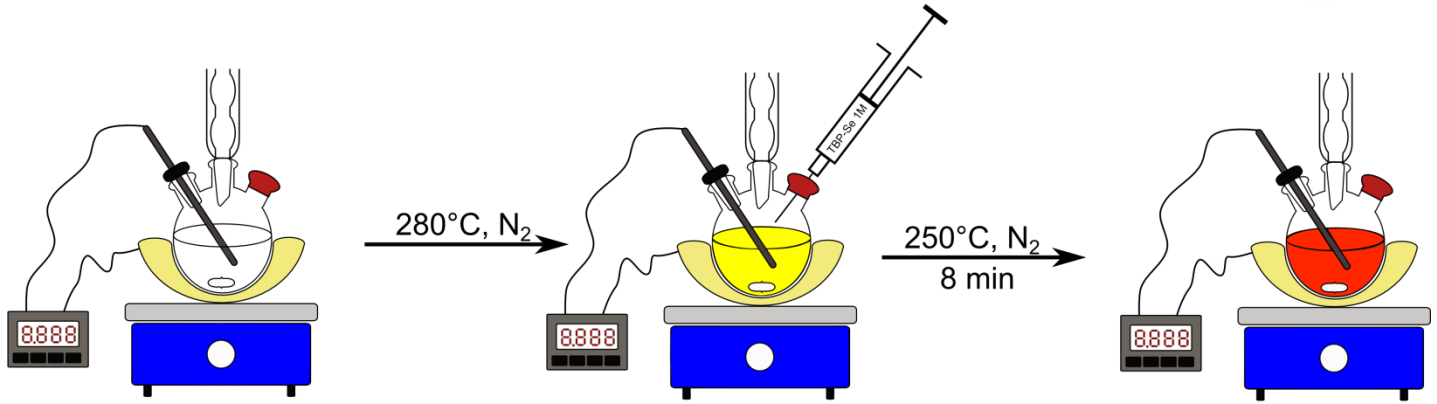
Quantum yield 60-70%





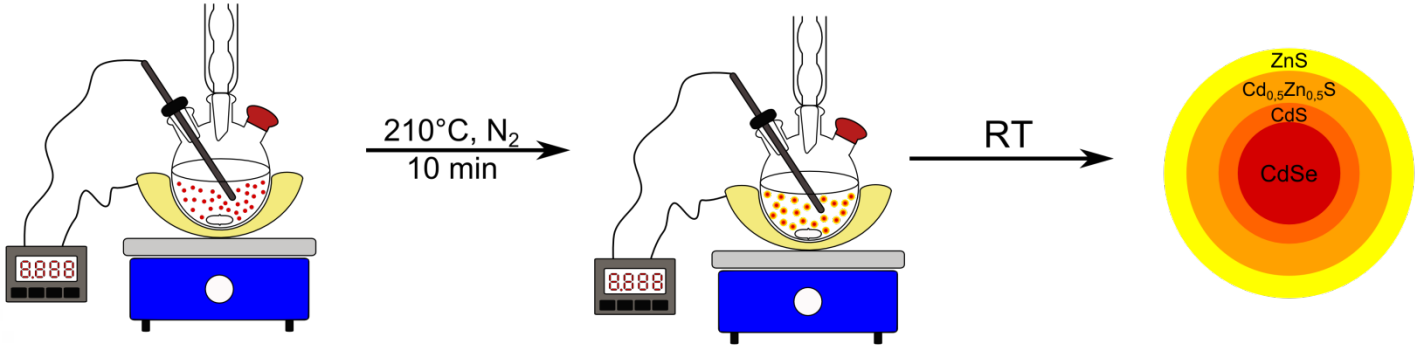
cQDs synthesis (SILAR method)

CdSe core



- Octadecene (ODE)
- TOPO 90%
- $Cd(OI)_2$ 0.5 M

Shell

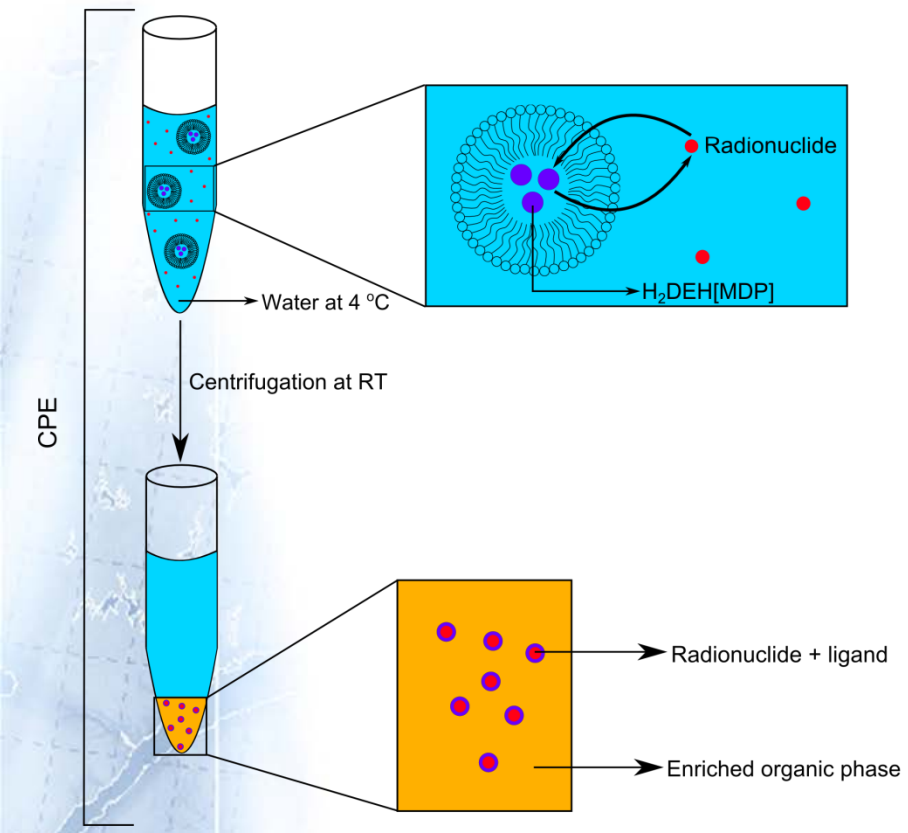


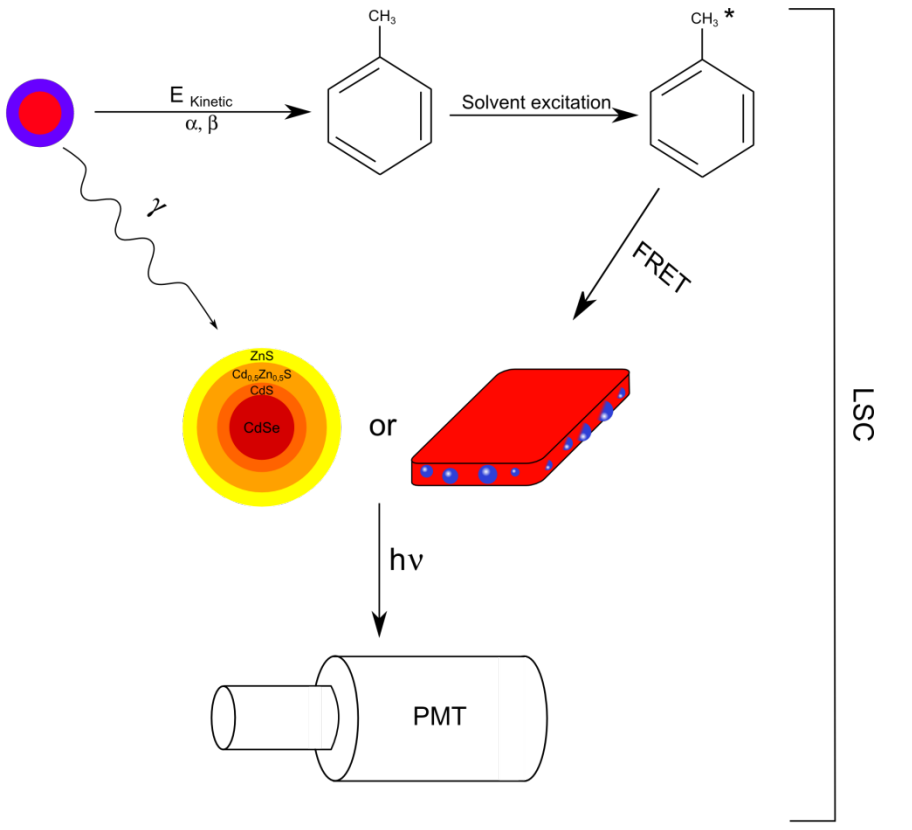
- ODE
- Oleylamine
- CdSe core

- Cd(OI)2 0.1 M
- Zn(OI)2 0.1 M
- S in ODE 0.1M

Li, J.J.; Wang, Y.A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M.B.; Peng, X. *J. Am. Chem.Soc.* **2003**, *125,*12567-12575.

Enhancement of medium interactions

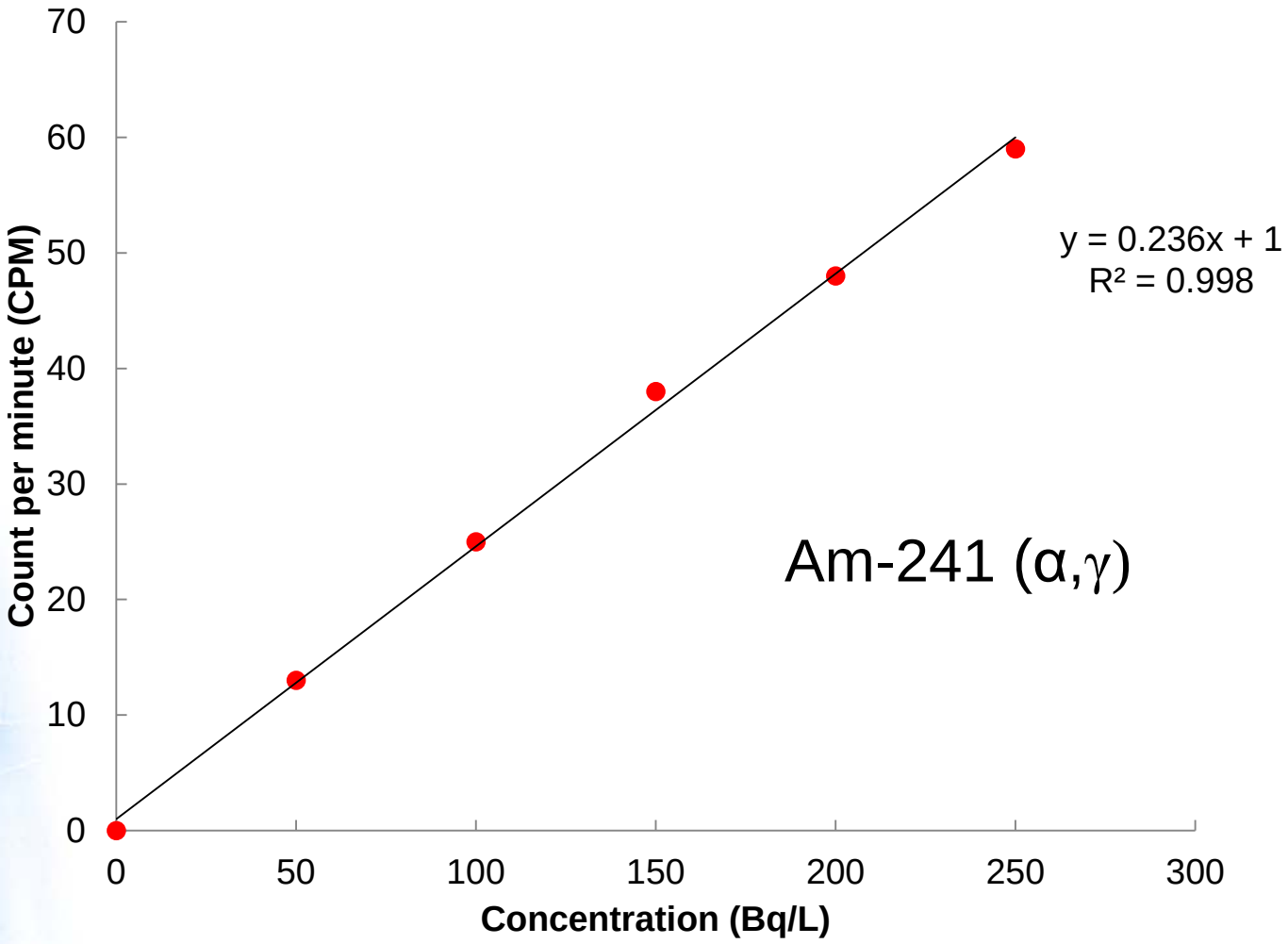




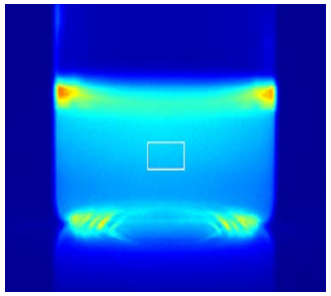
Labrecque, C.; Whitty-Léveillé, L.; Larivière, D. *Anal. Chem.* **2013**, *85*, 10549-10555.

Knoll, G.F. in Radiation detection and measurement, III ed.; Zobrist, B., Factor, K., Malinowski, S., Eds.; John Wiley and sons : New Jersey, 2000, p.220-247.

LSC results

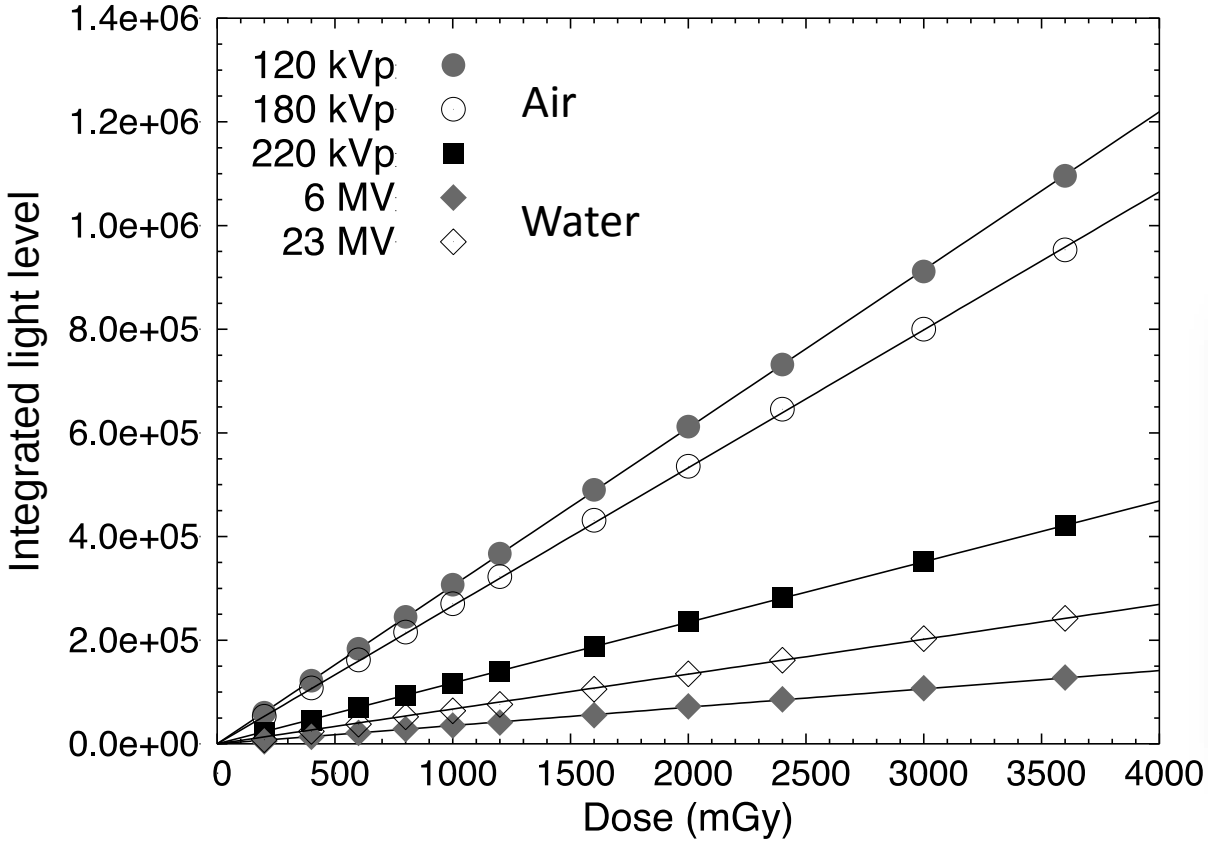

70
60
50
40
30
20
10
0
Count per minute (CPM)
0
50
100
150
200
250
300
Concentration (Bq/L)
y = 0.236x + 1
R² = 0.998
Am-241 (α,γ)

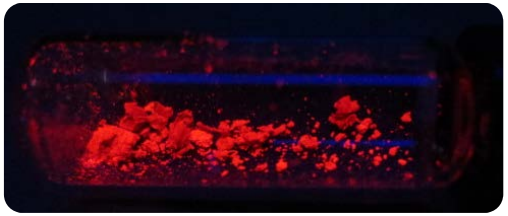
Gamma irradiation



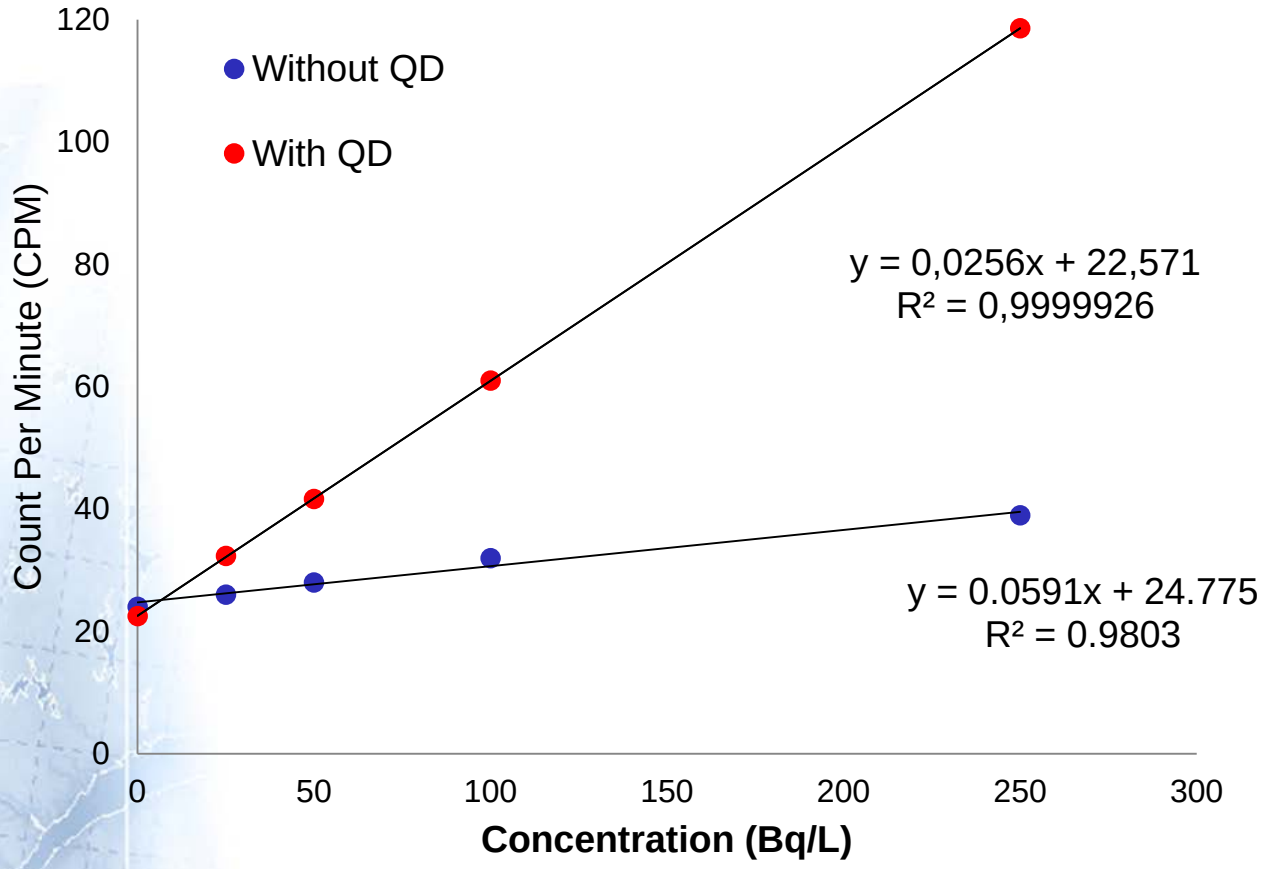
Lecavalier, M-E.; Goulet, M.; Allen, C.; Beaulieu, L.; Larivière, D. *Chem. Commun*. **2013**, *49*, 11629-11631.

Dosimetric applications





Calibration curve of Ra-226



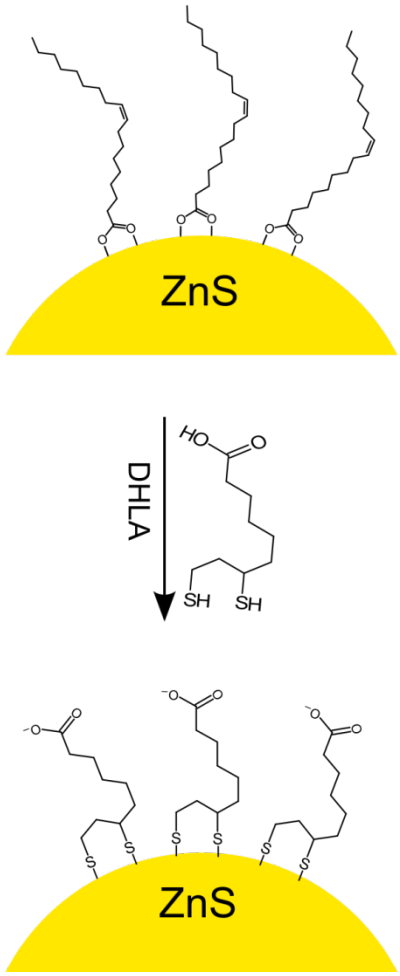


Figure 4: Calibration curve of Ra-226 with and without cQDs in borate buffer 25 mM at pH=8 with a concentration of 125 nM

Lecavalier, M-E.; Goulet, M.; Allen, C.; Beaulieu, L.; Larivière, D. *Chem. Commun*. **2013**, *49*, 11629-11631.

Room for improvement

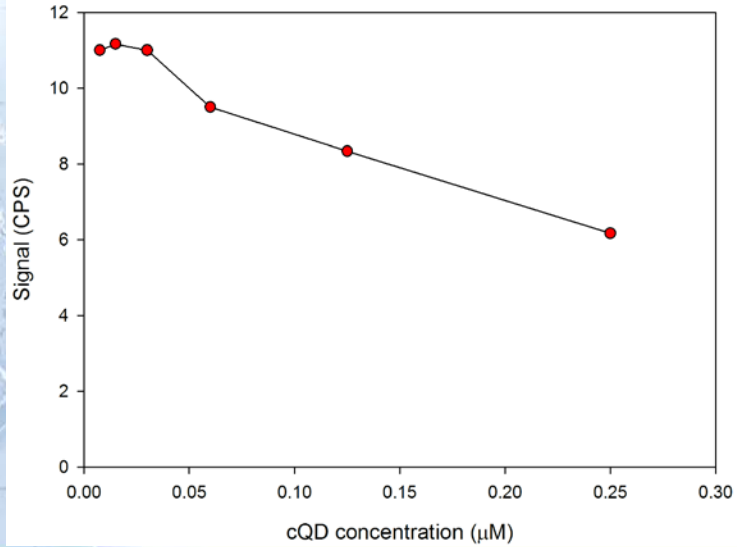
How cQDs might be improved :

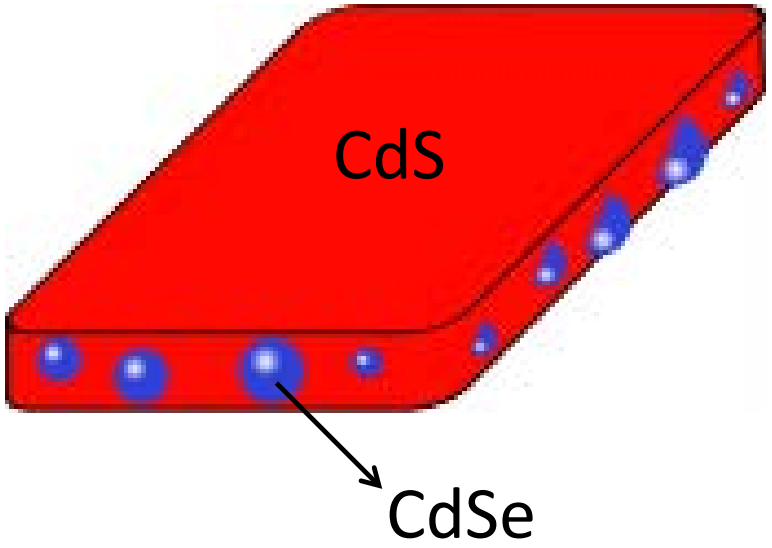
- Shorter fluorescence life time (compare to organic fluorophore)
- Higher quantum yield (compare to organic fluorophore)
- Emission in the PMT sensitivity range (compare to current cQDs)

Dots around nanoplatelets (DNPLs)

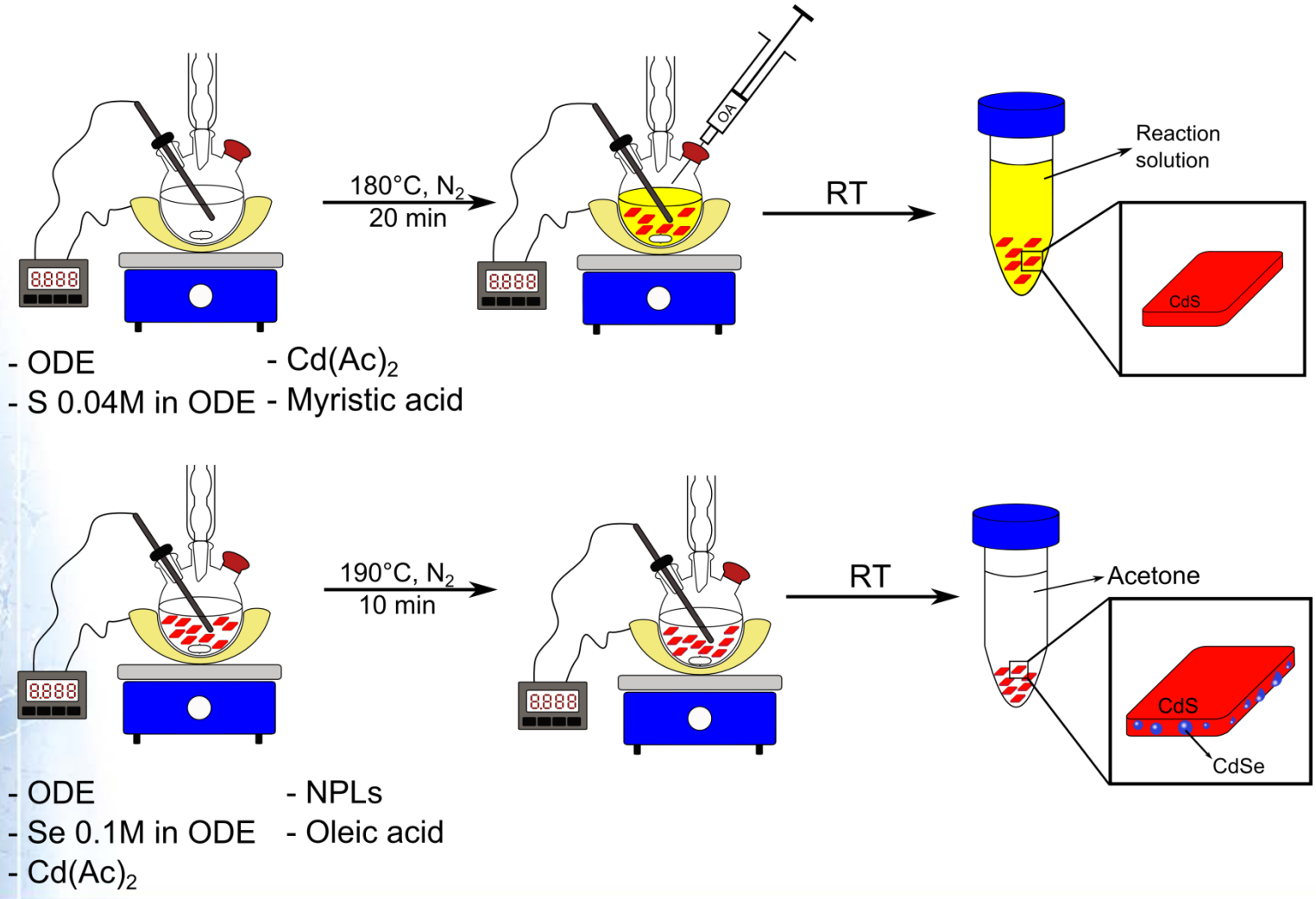
Forseen advantages:

- Emission wavelength in PMT sensitivity range
- High absorption cross section
- Multi-excitation
- Low reabsorption [CdSe]<[CdS]



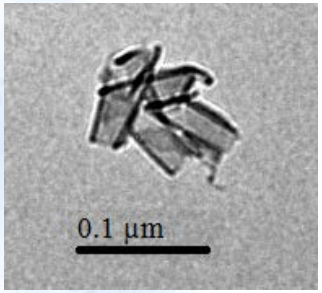


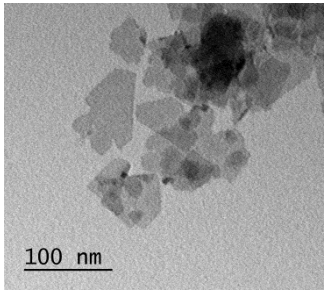
DNPLs Synthesis

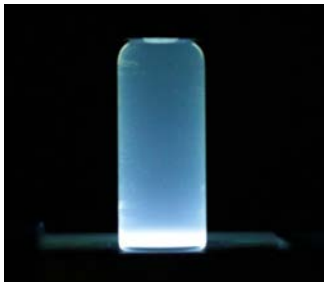


Li, Z.; Peng, X. *J. Am. Chem. Soc.* **2011**, *133*, 6578- 6586.

Characterization



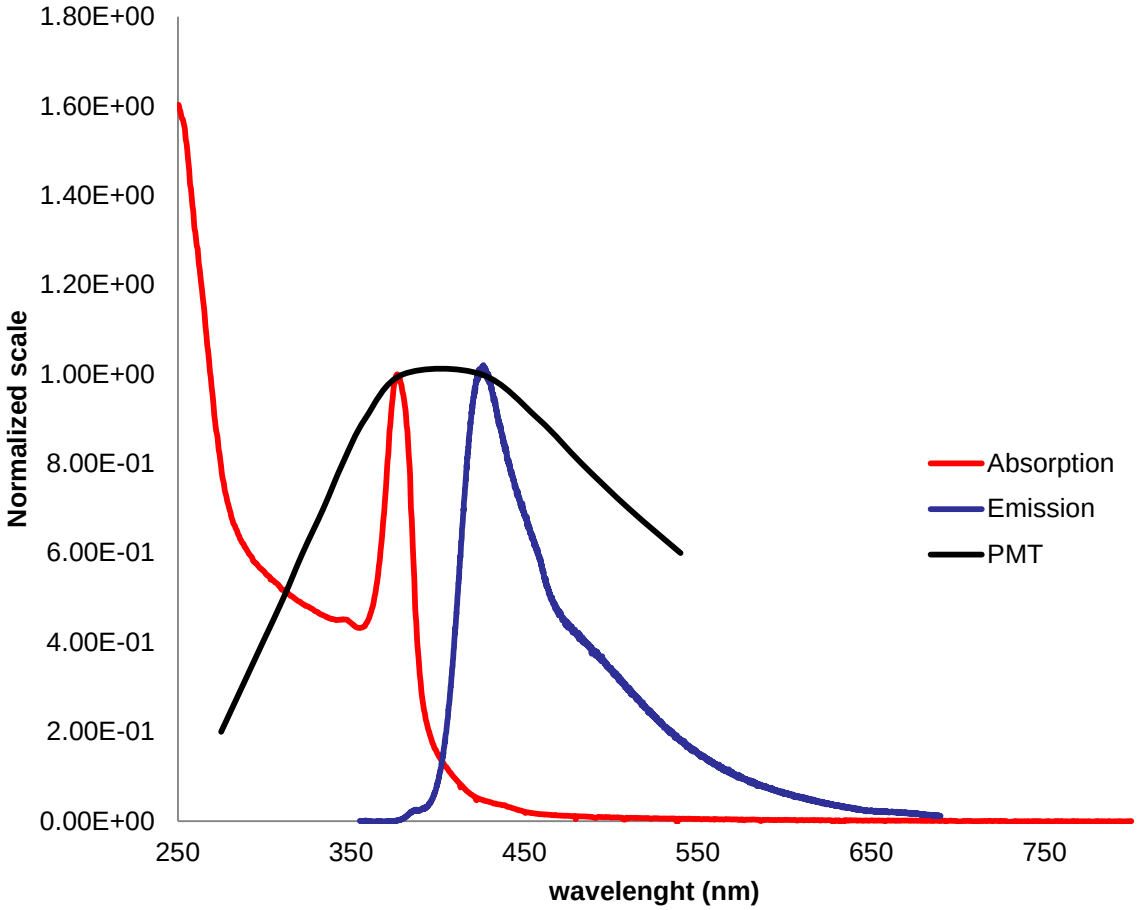




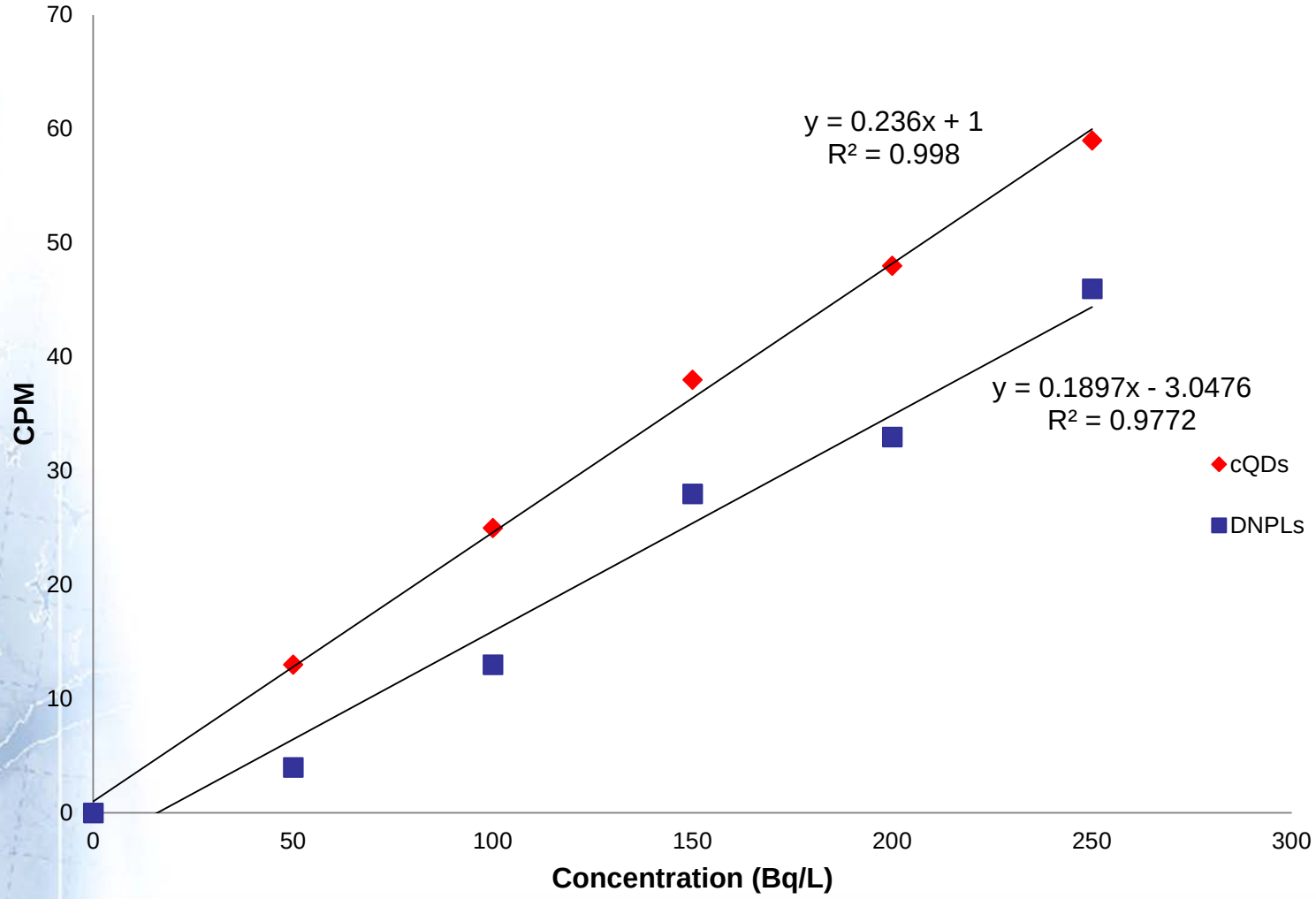
Initial Attempt (QY 3%)

Now

(QY 50%)



Calibration curve of Am-241



Radionuclides tested

Radionuclides	Counting efficiency of cQDs	Counting efficiency of DNPLs
	(%)	(%)
Am-241	28 ± 1	17 ± 5
Am-243	35 ± 6	35 ± 16
Th-230	23 ± 4	16 ± 9

Conclusion

- cQDs and DNPLs display interesting properties with regards to their possible use as solid scintillators or cocktails for liquid scintillation

- Both semi-conductor nanocrystals display possible applications as dosimeters

Future work

- Optimization of DNPLs for their use as scintillators
- Characterization of cQDs and DNPLs with X-rays, proton and electron beams
- Determination of other possible matrices (solid)
- Enhancement of the FRET between the solvent and cQDs/DNPLs

Acknowledgements

Ph.D student :
Marie-Ève Lecavalier (chemistry)
Marie-Eve Delage (physics)