Strongly inhibited spontaneous emission of near-IR PbS quantum dots in 3D silicon photonic band gap crystals

Andreas S. Schulz[1,2], Marek Kozoň[1,3], Jurriaan Huskens[2], G. Julius Vancso[4], and Willem L. Vos[1]

[1]*Complex Photonic Systems (COPS), MESA+ Institute, University of Twente, Enschede, The Netherlands*
[2]*Molecular Nanofabrication (MNF), MESA+ Institute, University of Twente, Enschede, The Netherlands*
[3]*Mathematics of Computational Science (MACS), MESA+ Institute, University of Twente, Enschede, The Netherlands*
[4]*Sustainable Polymer Chemistry (SPC), MESA+ Institute, University of Twente, Enschede, The Netherlands*

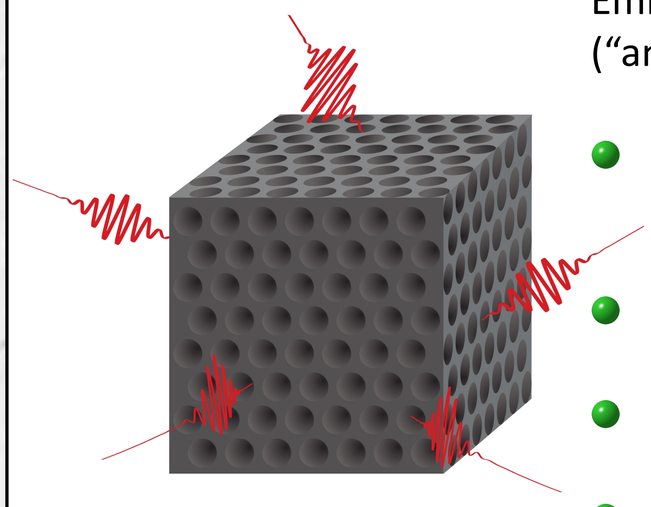
Introduction

Central in quantum optics and cavity quantum electrodynamics (cQED) ⇒ Control properties of matter via the properties of light!

- Famous: control radiative rate of elementary quantum emitters, like dye molecules, ions, or quantum dots (QDs) [1]
- Crucial for ***applications***: miniature *lasers* & *light-emitting diodes* [2], *photocatalysis* & *photochemistry* [3,4], and *sensing* [5,6]

Challenge: study ***emitters*** placed at ***well-defined positions*** in ***3D photonic band gap crystals***

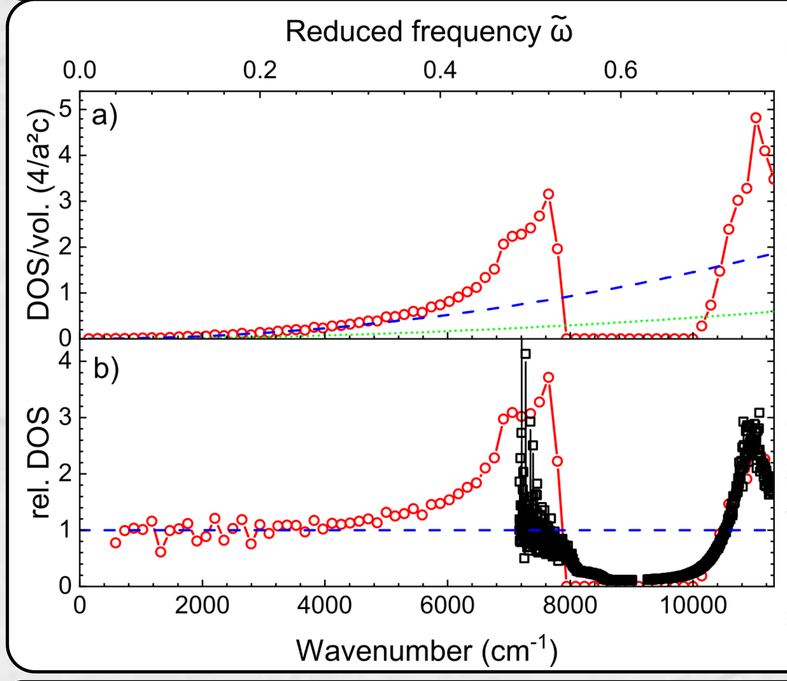
Vacuum Fluctuations & LDOS



Optical emitters typically in quantum regime ⇒ Emission induced by both radiative reaction (“antenna effect”) & by vacuum fluctuations [7]

- Vacuum fluctuations: fluctuations of quantized EM-fields (red wavelets), even in free space
- Combined effects captured by local density of radiative states (LDOS) [8]
- LDOS controlled by surrounding emitter by suitably tailored dielectric environment
- Most radical control: 3D photonic band gap: ***emission strongly inhibited***

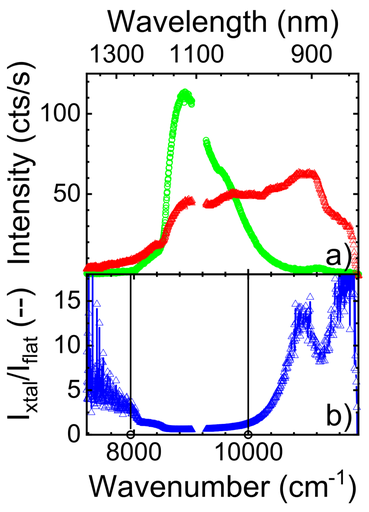
From Band Gap in Theory to Inhibition in Experiments

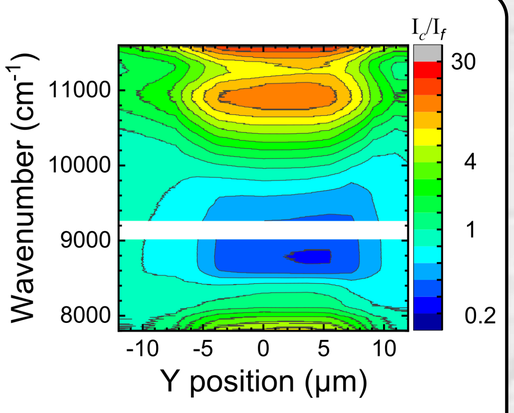


(a) Reduced density of states (DOS, a = lattice parameter, c = speed of light) for a 3D inverse woodpile photonic crystal from silicon, calculated for pores with radii R/a = 0.252 (red circles). Effective medium (blue); free space (green curve).

(b) Relative DOS equal to ratio of crystal and effective medium DOS (red circles).
Main result: measured intensity of QDs in the band gap crystal (black squares) normalized to similar QDs on a Si surface
⇒ Broad & deep ***gap*** apparent!

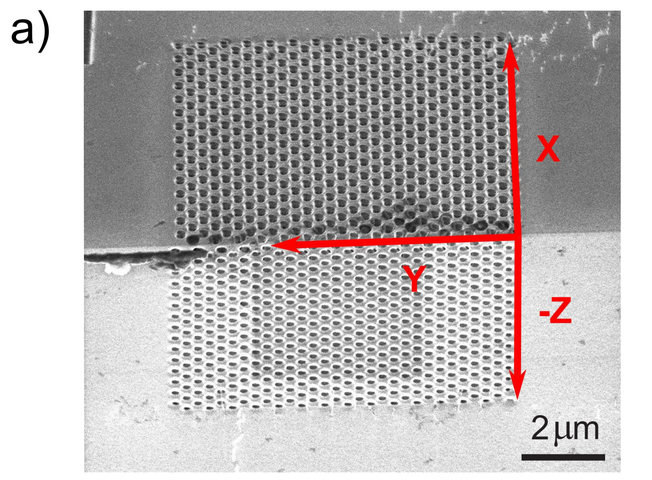
QD spectra in 3D PBG crystal (red) & on flat Si (green); ratio (blue)





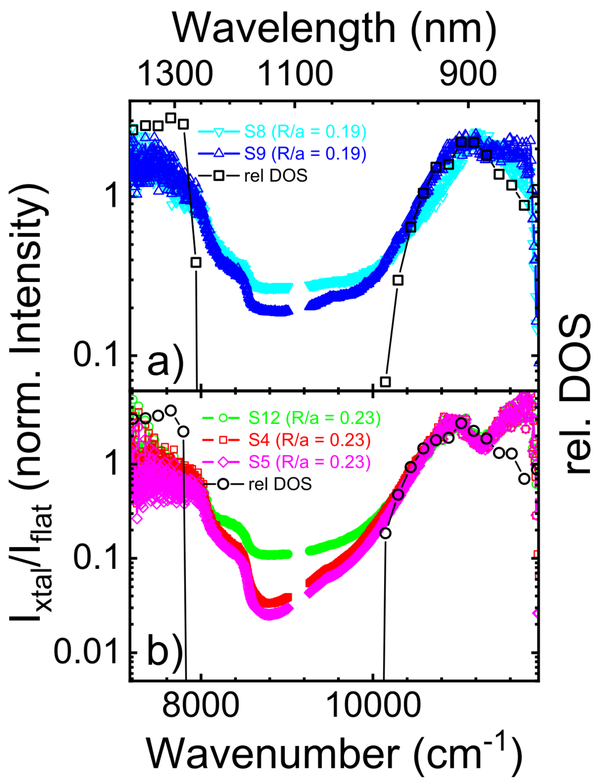
Spectral map of QDs in crystal: both ***inhibited & enhanced emission*** occur within the PBG crystal

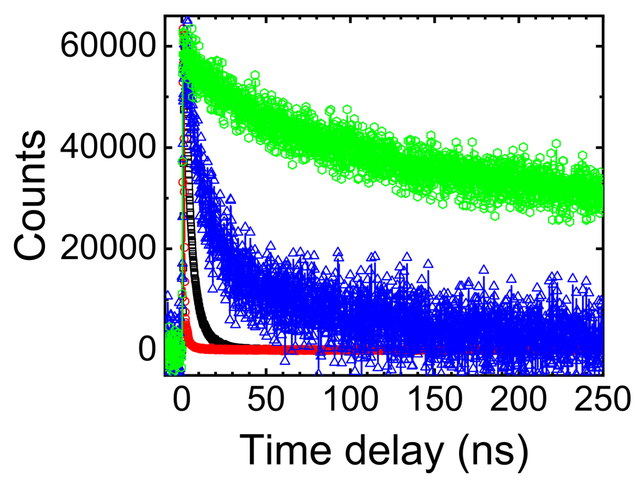
Our Photonic Crystals



(a) Scanning electron micrograph (SEM) of a 3D inverse woodpile photonic crystal (pore radii R=160 nm) made by us at MESA+
(b) Schematic of the unit cell, zooming in one a pore to show how we position QDs by targeted polymer surface-chemistry: ATRP initiator layer (orange), polymer chains forming brushes (green), covalently attached PbS quantum dots (black) on silicon (blue). The positioning was verified by X-ray fluo tomography [9].

Strongly Inhibited Emission





Time-correlated single photon counting of PbS QDs on flat Si (black squares), in crystal S4 (blue triangles), crystal S12 (red circles), in suspension (green hexes @1090 nm). Counts plotted vs photon arrival time.

Normalized emission spectra of QDs in several 3D crystals, see central panel.
(a) With pore radii R/a=0.19: S9, S8
(b) With pore radii R/a=0.23: S4, S12, S5
Calculated relative DOS for relevant pore radii (connected black symbols)
Excellent reproduction between different crystals with same pore radii.
Systematic shift of the band gap with varying crystal dimensions

References

[1] A.F. Koenderink, *et al*., PRL **88** (2002) 143903; P. Lodahl, …, D. Vanmaekelbergh & W.L. Vos, Nature **430** (2004) 654
[2] E. Yablonovitch, Inhibited Spontaneous Emission in Solid-State Physics and Electronics, Phys. Rev. Lett. **58** (1987) 2059-2062
[3] S. Nishimura *et. al.*, Journal of the American Chemical Society **125** (2003) 6306–6310
[4] H. Li, R. Liu, S. Lian, Y. Liu, H. Huang, Z. Kang, NANOSCALE **5** (2013) 3289–3297
[5] M.F. Frasco, N. Chaniotakis, Semiconductor Quantum Dots in Chemical Sensors and Biosensors, Sensors **9** (2009) 7266–7286
[6] M. Li, T. Chen, J.J. Gooding, J. Liu, ACS Sensors **4** (2019) 1732–1748
[7] P.W. Milonni, The Quantum Vacuum: an Introduction to Quantum Electrodynamics; Academic Press, Boston, 1994
[8] W.L. Barnes, S.A.R. Horsley, W.L. Vos, Journal of Optics **22** (2020) 073501
[9] A. S. Schulz, C.A.M. Harteveld, G.J. Vancso, J. Huskens, P. Cloetens & W.L. Vos, ACS Nano **16** (2022) 3674
[10] Schulz *et. al*., Strongly Inhibited Spontaneous E., ChemRxiv, www.chemrxiv.org/engage/chemrxiv/article-details/6531fdef87198ede07d89592