Quantum-Confined and Enhanced Optical Absorption of Colloidal PbS Quantum Dots at Wavelengths with Expected Bulk Behavior

Doriana Debellis,[a] Giuseppe Gigli,[a,b] Stephanie ten Brink,[c] Ivan Infante,[c] Carlo Giansante[a,b,*]

[a] *Dipartimento di Matematica e Fisica 'E. De Giorgi', Università del Salento, via per Arnesano, 73100 Lecce, Italy*
[b] *NANOTEC-CNR Istituto di Nanotecnologia, via per Arnesano, 73100 Lecce, Italy*
[c] *Department of Theoretical Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands*
* carlo.giansante@unisalento.it

Nowadays it is well-accepted to attribute bulk-like optical absorption properties to colloidal PbS quantum dots (QDs) at wavelengths above 400 nm. This assumption permits to describe PbS QD light absorption by using bulk optical constants and to determine QD concentration in colloidal solutions from simple spectrophotometric measurements.[1,2]
Here we demonstrate that PbS QDs experience the quantum confinement regime across the entire near UV-vis-NIR spectral range, therefore also between 350 and 400 nm already proposed to be sufficiently far above the band gap to suppress quantum confinement. This effect is particularly relevant for small PbS QDs (with diameter of ≤4 nm) leading to absorption coefficients that largely differ from those expected from bulk values (up to ~40% less; black open squares in Fig. 1).
As a result of the broadband quantum confinement, the high surface-to-volume ratio and the inherent ligand/core orbital mixing peculiar of nanocrystals,[3] suitable surface chemical modification of PbS QDs is exploited to achieve a marked, size-dependent enhancement of the absorption coefficients compared to bulk values (up to ~250%; red symbols in Fig. 1).

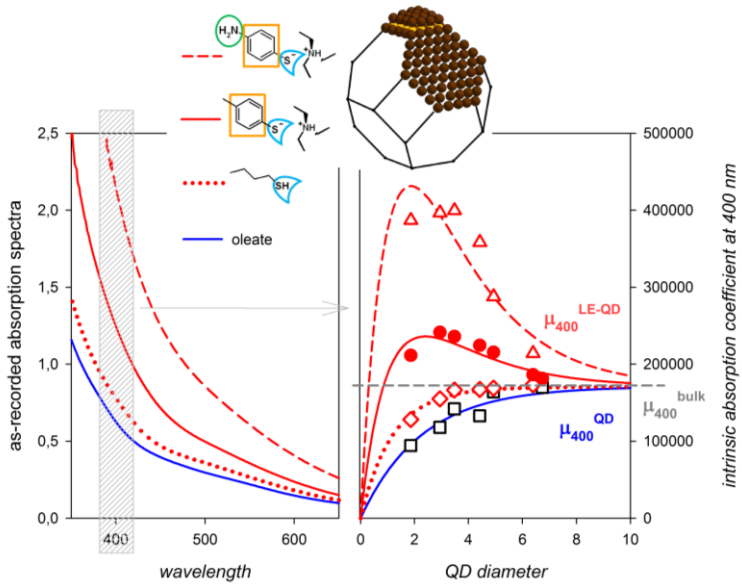

Fig. 1 Intrinsic (per material unit) absorption coefficients at 400 nm for as-synthesized and ligand-exchanged colloidal PbS QDs showing deviations from the (previously) expected bulk value.

We provide empirical relations to determine the absorption coefficients at 400 nm of as-synthesized and ligand-exchanged PbS QDs, accounting for the broadband quantum confinement and suggesting a heuristic approach to qualitatively predict the ligand effects on the optical absorption properties of PbS QDs. Our findings go beyond formalisms derived from Maxwell Garnett effective medium theory to describe QD optical properties and permit to spectrophotometrically calculate the concentration of PbS QD solutions avoiding underestimation due to deviations from the bulk.
In perspective, we envisage the use of extended π-conjugated ligands bearing electronically active substituents to enhance light-harvesting in QD solids and suggest the inadequacy of the representation of ligands at the QD surface as mere electric dipoles.

1) I. Moreels *et al.*, *ACS Nano*, **2009**, *3*, 3023.
2) Z. Hens, I. Moreels, *J. Mater. Chem.*, **2012**, *22*, 10406.
3) C. Giansante *et al.*, *J. Am. Chem. Soc.*, **2015**, *137*, 1875.