Semiconductor Nanoplatelet Excimers

Diroll, B.T., Cho, W., Coropceanu, I., Harvey, S.M., Brumberg, A., Holtgrewe, N., Wasielewski, M.R. and Schaller, R.D. (Argonne National Lab & Northwestern University); Crooker, S.A. (NHMFL-Los Alamos); Prakapenka, V.B. and Talapin, D.V. (University of Chicago)

Introduction

Colloidal nanoplatelets (NPLs) are two-dimensional materials with an atomically precise thickness that dominates quantum confinement. These materials elicit great interest for light-emitting applications and have demonstrated promise as laser gain media. Strong van der Waals interactions drive a propensity to form cofacial assemblies that exhibit strong inter-NPL interactions, such as fast Förster resonant energy transfer (FRET). Excimer ("excited dimer") formation is a process related to FRET in which a delocalized excited state is formed from an excited fluorophore and an unexcited neighbor, evidenced by redshifted emission with no corresponding absorption feature. Although common in aromatic organic crystals, which also present homogeneous electronic structure and cofacial alignment, such emergent electronic structure has not been identified in colloidal semiconductor nanocrystals, although small metallic clusters are reported to form excimers and two-dimensional materials are known to from charge-separated "interlayer excitons".

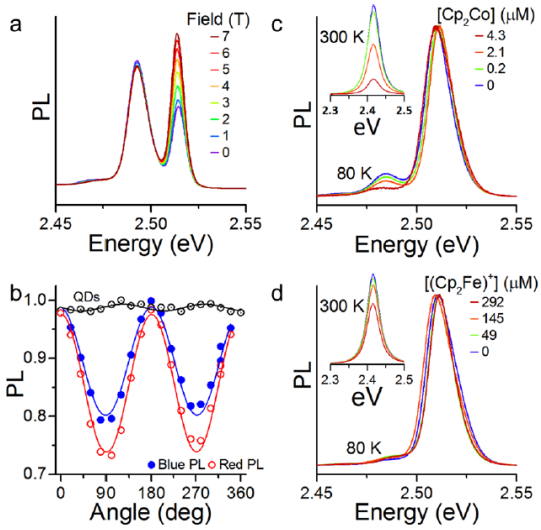

Figure: (a) Magnetic field dependence of PL from a sample of 4 ML CdSe NPLs at 4 K. (b) Emission polarization-dependent PL from the blue and red PL features of a 4 ML NPL in a stretched polymer film at 80 K. Unpolarized quantum dots (QDs) show the residual instrumental polarization. (c) PL of 4 ML frozen NPL solutions at 80 K in toluene with specified amounts of cobaltocene [Cp2Co], normalized to the blue PL feature with un-normalized 300 K data inset. (d) PL of 4 ML frozen NPL solutions at 80 K in toluene with specified amounts of ferricinium hexafluorophosphate [(Cp2Fe)(PF6)], normalized to the blue PL feature, with un-normalized 300 K data inset.

Results and Discussion

Excimers, a portmanteau of "excited dimer", are transient species that are formed from the electronic interaction of a fluorophore in the excited state with a neighbor in the ground state, which have found extensive use as laser gain media. Although common in molecular fluorophores, this work presents evidence for the formation of excimers in a new class of materials: atomically precise two dimensional semiconductor nanoplatelets. Colloidal nanoplatelets of CdSe display two-color photoluminescence resolved at low temperatures with one band attributed to band-edge fluorescence and a second, red band attributed to excimer fluorescence. Previously reasonable explanations for two-color fluorescence, such as charging, are shown to be inconsistent with additional evidence. As with excimers in other materials systems, excimer emission is increased by increasing nanoplatelet concentration and the degree of cofacial stacking. Consistent with their promise as low-threshold gain media, amplified spontaneous emission emerges from the excimer emission line.

Photoemission from CdSe NPL ensembles at temperatures below 100 K is known to consist of two closely spaced bands, here termed "blue" and "red" for high- and low-energy features, respectively. Several different explanations for this multistate PL exist in the literature, including band-edge and phonon line emission, band-edge and trion emission, or s- and excited p-state exciton emission. In this work, we revisit earlier findings and present new experimental data that contradicts these otherwise reasonable prior interpretations. Instead, data on PL dynamics, polarization, and sensitivity to microstructure support an explanation of two-state emission in which blue emission arises from the band-edge s exciton state, while the red emission arises from an excimer-like state emergent from the collective electronic structure of neighboring NPLs. In particular, the red PL feature shows strong sensitivity to pressure, NPL concentration, and self-assembly into cofacial stacks which is emblematic of excimer emission in molecular fluorophores.

References

[1] Diroll, B. T. *et al.*, Nano Letters **18**, 6948-6953 (2018).