Excitons in Ultrathin Exfoliated Small Molecule Crystalline Thin Films

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Over the past ten years, the success of solution-based deposition techniques for small molecule semiconductors led to exciting new avenues for exploration of many body interactions in soft matter. Of particular interest are molecules where the short-range π-stacking and long-range intermolecular Coulomb interaction are on equal footing with the reorganization energy. The Furis group has extensively studied the formation of delocalized excitonic states when the static disorder is largely eliminated thanks to a meniscus-guided deposition technique.

Here we report on the first experiments conducted in pure, defect free single-crystal ultrathin films obtained by mechanical exfoliation of solution-deposited thin films with macroscopic ordering. The exfoliation procedure

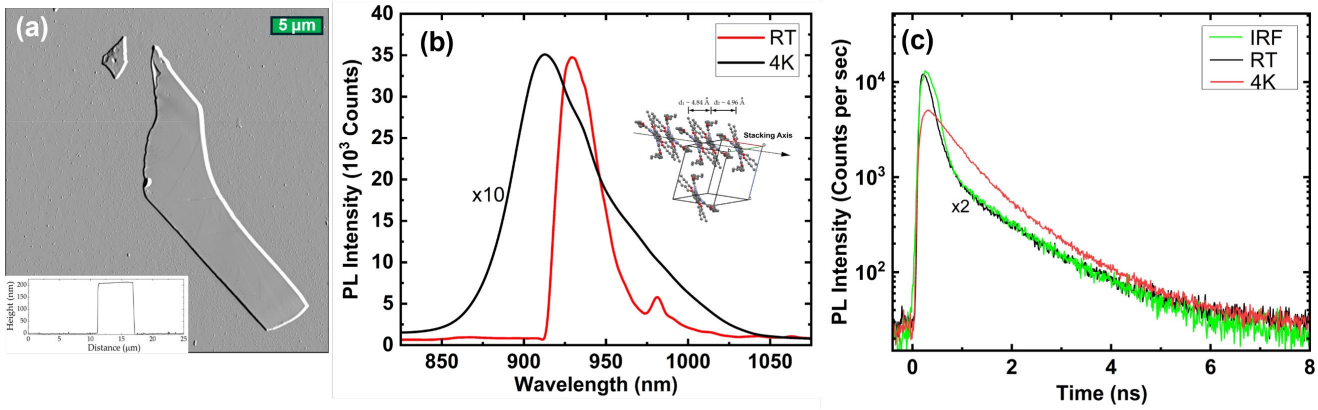

Fig.1. (a) Atomic force microscopy (AFM) image of a crystalline, flat octabutoxy-phthalocyanine (H_2OBPc) flake obtained by exfoliation of solution deposited thin films. The inset is a cross-section through the AFM image illustrating thickness is uniform across the flake width. (b) Photoluminescence spectra recorded form a single-crystalline flake at 4 K and room temperature (RT). The inset shows the molecules stacking in the crystalline flake, which results in delocalized excitonic states and bright near-infrared emission at low temperature. (c) Photoluminescence decay recorded at the peak emission wavelengths extracted from the PL spectra in panel (b).

was accomplished using PDMS films which leaves little residue and resulted in chemical-stable, large flakes suitable for optical microscopy, as shown in Fig. 1a. An example of a single-flake photoluminescence (PL) spectrum is shown in Fig 1b. At low temperatures we observe bright, spectrally narrow emission and a weak, suppressed phonon replica. These are the signatures of coherent, delocalized excitonic state formation. The emission is red shifted by 100 nm compared to the molecules emission in dilute solution. [1] These excitons are very short lived (see fig.1c), a signature of delocalization. A comprehensive flake thickness dependence survey was performed using correlated AFM and PL measurements to establish the evolution of excitonic properties. The flakes ranged in thickness from 600 nm to 20 nm. The thinnest flakes only have 12 molecular layers.

With decreasing flake thickness, the exciton energy decreases while the full width at half maximum (FWHM) increases. This behavior can be assigned to the different mechanical strain that flakes may be experience after transfer on the sapphire substrate. The most remarkable result is the suppression of phonon replicas in the thinnest flakes which possibly indicates the decoupling of excitons from the lattice vibrations, a highly desirable outcome that favors the formation of coherent excitons at elevated temperatures.

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References

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