

Luminescence from Isolated Tb-based Metallacrown Molecular Complexes on *h*-BN

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The interest in single molecule spectroscopy has been long hindered by the challenging detection of weak signals, whose spectra are highly environment-dependent and prone to ensemble broadening. The family of luminescent lanthanide(III)-based metallacrown (MC) complexes are promising systems that demonstrate tunable emission bands that span the visible to the near-infrared spectrum. In the case of Ga^{3+}/Ln^{3+} MC complexes ($Ln = Tb, Dy, Eu, Yb$) with a 12- $MC_{Ga(III)shi}^{-4}$ core about the central Ln -atom, such as $TbGa_4shi_4$ ($shi = \text{salicylhydroximate organic ligand}$), it demonstrates characteristically sharp $4f-4f$ transitions in the visible in both solid-state and in solution [1]. These MCs are molecular magnets whose excited states could in principle be accessed by light. The study of the luminescence of individual molecules will provide fundamental insights on their electronic structure that ultimately determine their magnetic properties. Scanning transmission electron microscopes (STEM) can be the platform to combine the different imaging and spectroscopic capabilities at the scale of single molecules. High-angle annular dark-field (HAADF) Z-contrast imaging in an aberration-corrected STEM can be well-adapted to observing individual molecules given the heavy atoms within the MC core. Excitation of single molecules by way of a wide-bandgap substrate like hexagonal boron nitride (*h*-BN) using cathodoluminescence in a STEM (nanoCL) provides significant advantages over existing near-field techniques.

In this contribution, the low-temperature luminescence of $TbGa_4shi_4$ MCs deposited in dilute concentrations on high-purity *h*-BN flakes with known intrinsic and defect luminescence is explored using a random scan approach [2] to limit dose accumulation effects on a VG HB501 STEM. The distribution of isolated molecules on *h*-BN is determined using a Nion UltraSTEM200 operated at 60 keV. STEM-HAADF images [Fig. 1(a,b)] show a high density of high-Z single atoms and few-atom clusters expected of single or di-molecules, in addition to the presence of carbonaceous material decorating the BN flake edges. With further dilution, the ratio of atomic clusters to single atoms decreases, and their separation increases to tens of nm [Fig. 1(c)]. The presence of molecules introduces various emission lines in the range of 2.0–3.5 eV not present in pristine *h*-BN [Fig. 1(d), Fig. 2(a)], some with narrow linewidths and others in pairs or triplets that do not match exactly coupling with *h*-BN phonons. Their emission maps exhibit spotty spatial localization down to widespread single pixels of 10 nm in size [Fig. 1(e)]. Moreover, the random scan enables the segmentation of the spectrum image into time slices [2], which uncovers the emission dynamics transitioning from 3.23 eV to the anti-correlated 3.02 eV [Fig. 2(c)], suggestive of electron-beam induced modification to the molecule. Lastly, complementary electron energy-loss spectroscopy (EELS) on the single molecules will also be discussed [3].

References:

[1] C Y Chow et al., JACS **138** (2016), p. 5100.

[2] A Zobelli et al., in preparation.

[3] The authors acknowledge funding from the ANR, program of future investment TEMPOS-CHROMATEM (No. ANR-10-EQPX- 50). SYW acknowledges NSERC for the fellowship funding.

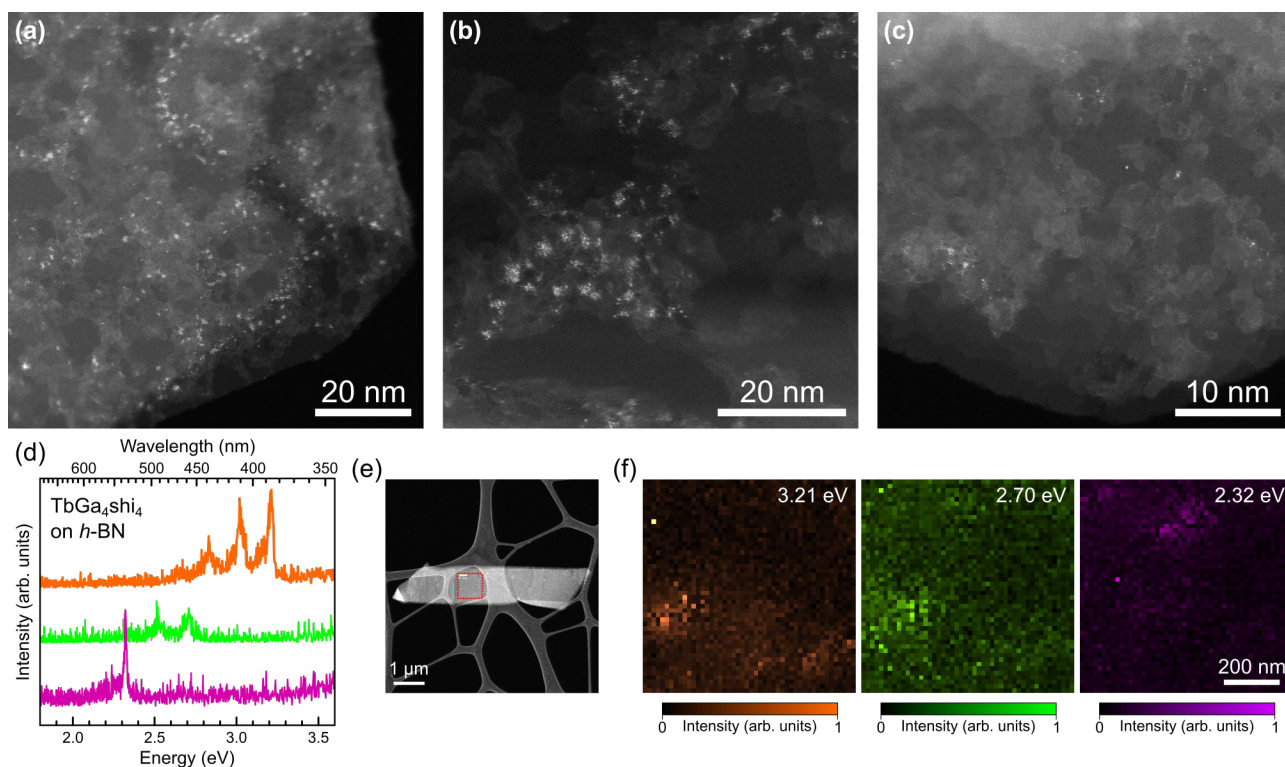


Figure 1. (a–c) STEM-HAADF images of $\text{TbGa}_4\text{shi}_4$ molecules on *h*-BN seen as the high-*Z* few-atom clusters, and in (c) with further dilution representative of sample used for nanoCL study. CL spectrum imaging of molecules on *h*-BN: (d) CL spectra, (e) HAADF image, and (f) intensity maps.

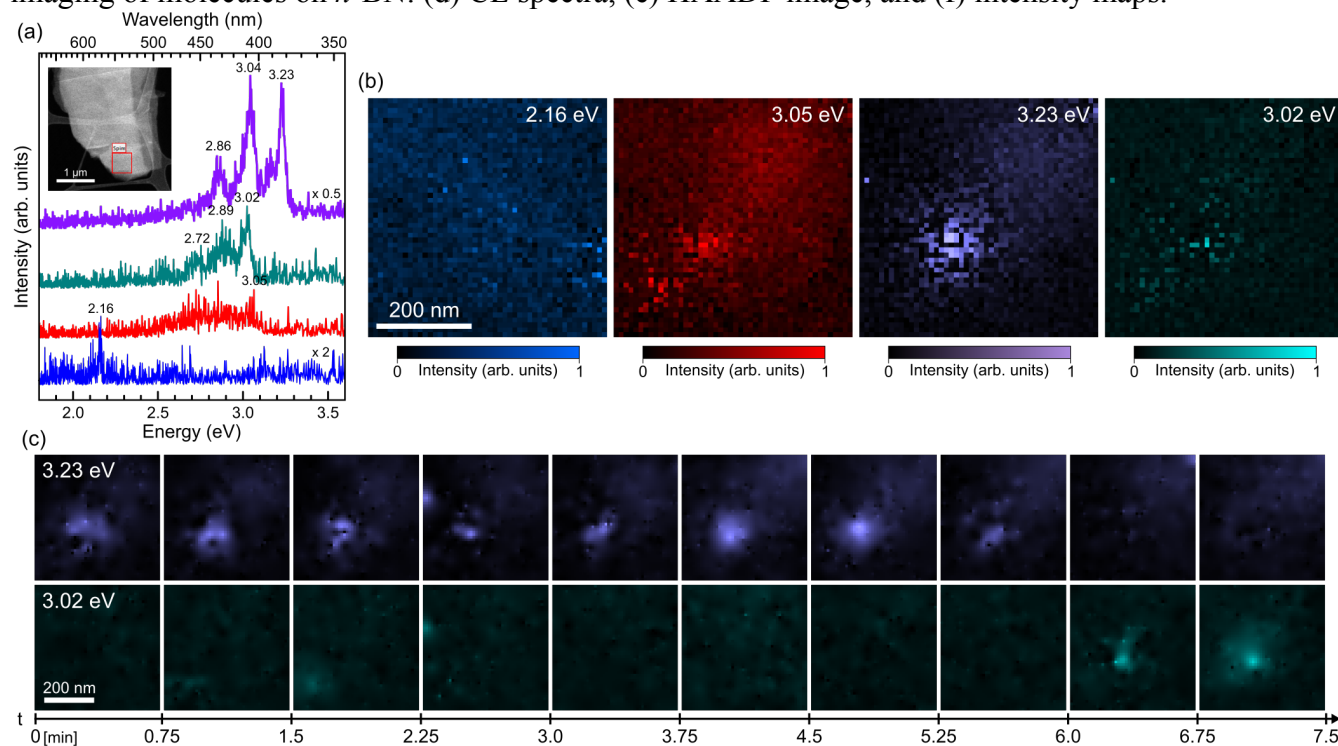


Figure 2. CL spectrum imaging with random-scanning: (a) CL spectra, (b) intensity maps, and (c) time-sequenced reconstructed CL maps of the 2 emission lines from segmentation of the spectrum image demonstrating spectral diffusion after ~ 6 min.