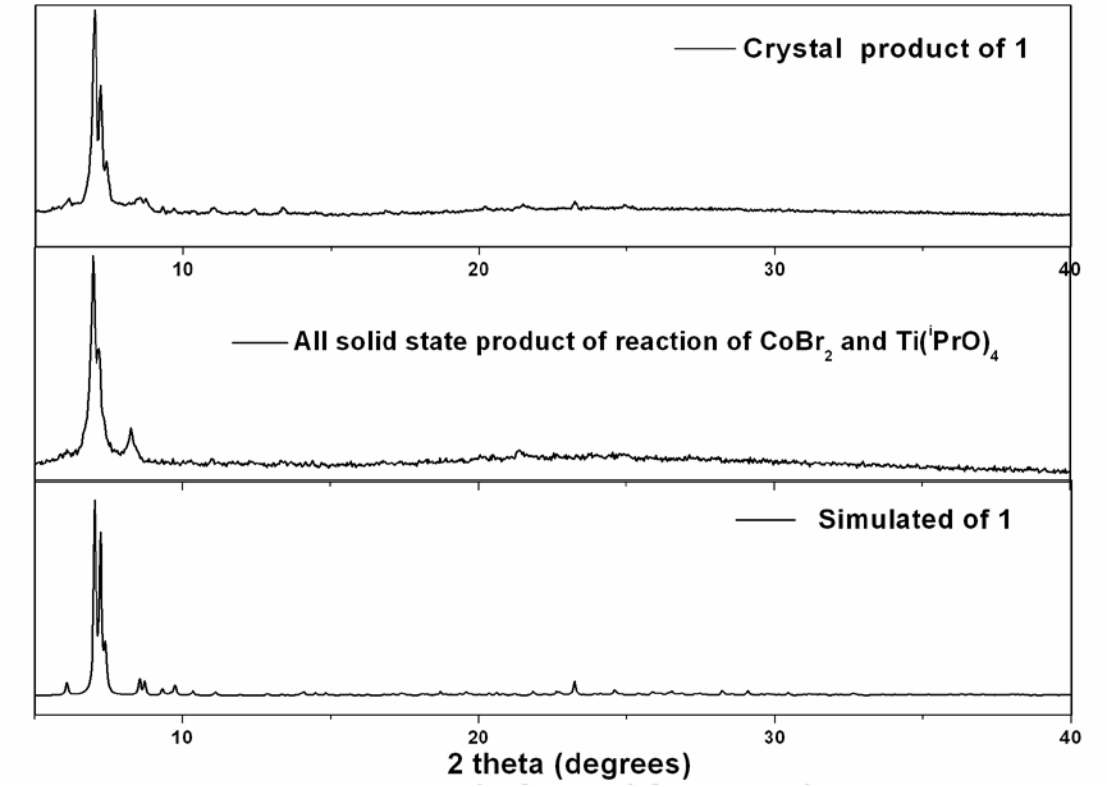
ESI

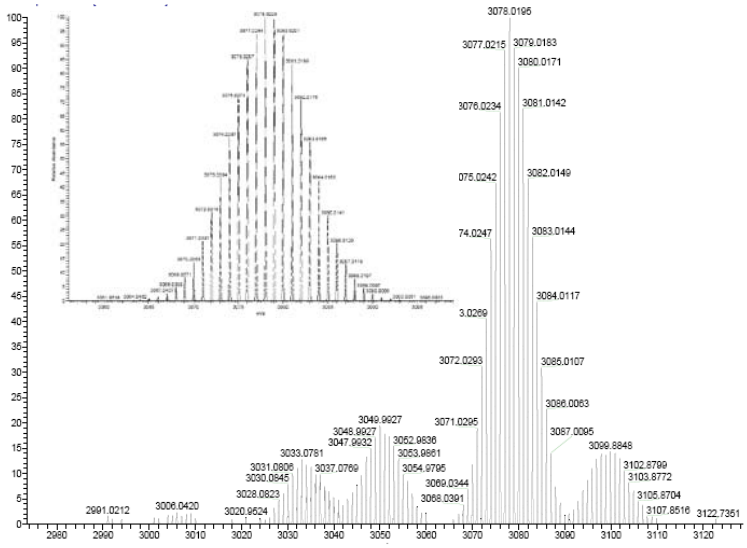
X-ray Powder Diffraction of 1

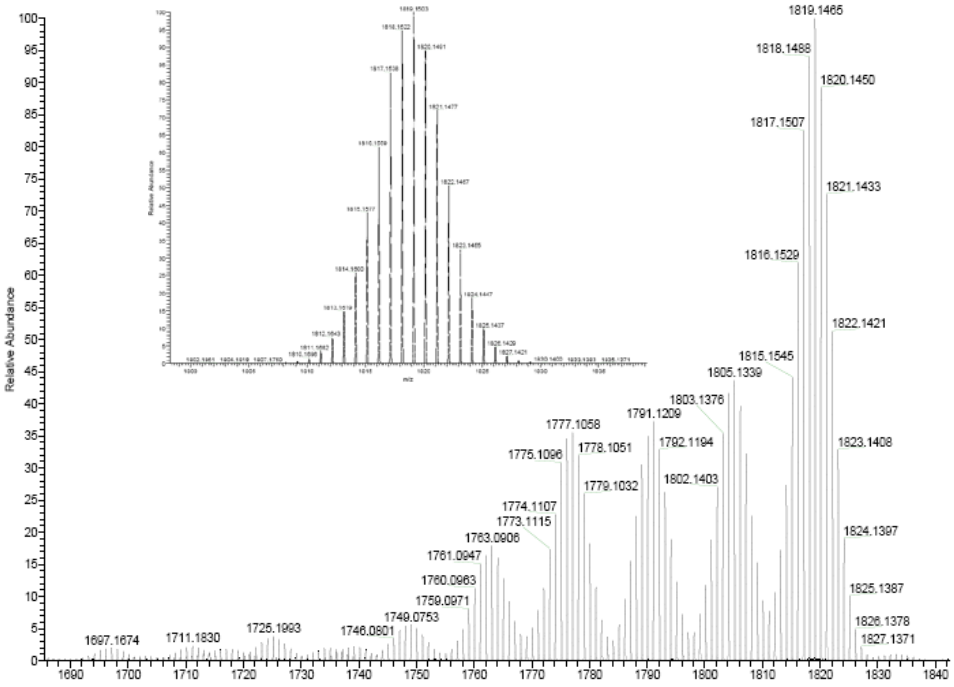
X-ray powder diffraction was performed using a PANalytical X'Pert PRO MPD system (PANalytical B.V., The Netherlands) with Cu Kα radiation (λ = 1.542 Å). The X-ray generator was set to an acceleration voltage of 40 kV and a filament emission of 40 mA.



Mass Spectrometry

The –ve and +ve ion mass spectra were obtained on a Thermo Fischer Scientific mass spectrometer using a voltage of 4.03 V, a vaporization temperature of -59.6^{o}C and a capillary voltage of 274.9V. The mass spectra are shown below. The inserts are the calculated envelopes for the ions.



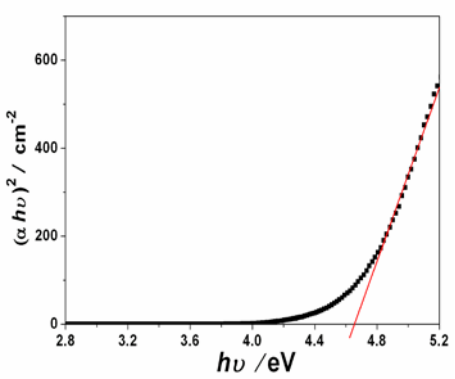


Band-gap Calculations from UV-visible data

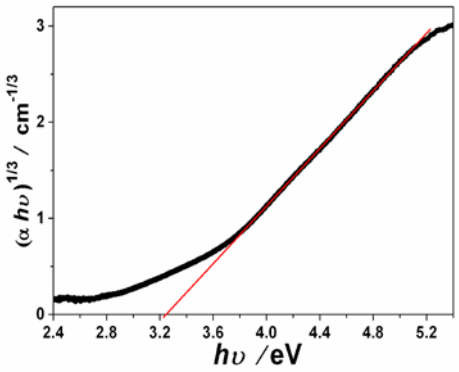
UV-visible spectra were recorded using a Cary 50 probe Varian uv-visible spectrometer. For optical transitions near the absorption edge the absorption coefficient α (in cm^{-1}) is given by the equation,

Where B is the absorption constant for the transition, E_g (in eV) is the bandgap, and hν (in eV) is the photon energy. The exponent n characterizes the nature of the transition For allowed direct and indirect transitions n = 0.5 and 2.0, respectively, whereas for forbidden direct and indirect transitions n = 1.5 and 3.0, respectively. (S. Adachi, *Optical Properties of Crystalline and Amorphous Semiconductors; Materials and Fundamental Properties*, Kluwer, Norwell MA, 1999, p. 280)

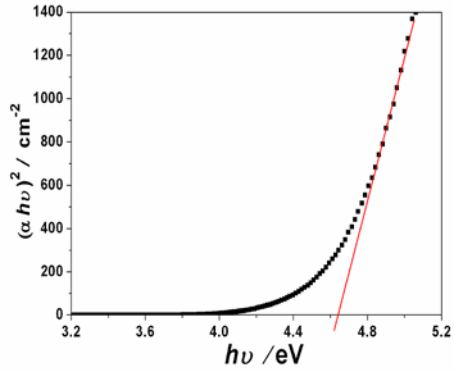
The UV-visible data was modeled around the absorption edge using a linear correlation (as shown below).



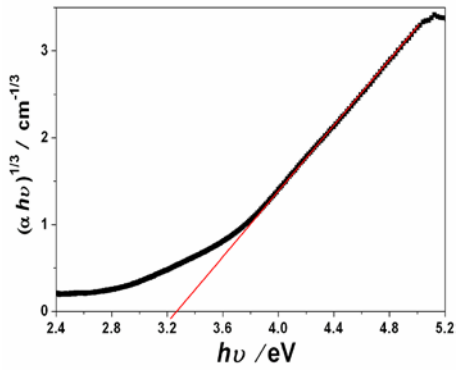
direct 0.0413g/L band gap 4.65



indirect 0.0413g/L band gap 3.23



direct 0.0825g/L band gap 4.64



indirect 0.0825g/L band gap 3.24

Linear correlations for direct allowed (n = 0.5) (R = 0.99, left) and indirect forbidden (n = 3) (R = 0.99, right). As the concentration was increased above *ca.* 0.08 g L^{-1} the calculated indirect band-gap remains the same at all of the concentrations investigated (see Fig. 4). However, the calculated direct band-gap decreases with increased concentration. The sensitivity of the direct band-gap calculation to concentration is explained by the effect of scattering due to particle/aggregate formation as the concentration increases, combined with the inherently greater mathematical sensitivity of the direct band gap calculation, according to equ. 1 (n = 0.5) as opposed to indirect (n = 3).