Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Solution phase synthesis of the less-known Form II crystalline red phosphorus

*Zhaojian Sun‡, Bowen Zhang‡, and Qingfeng Yan**

Department of Chemistry, Tsinghua University, Beijing 100084, China

Figure S1. Photograph of the Form II RP product synthesized by solvothermal reaction.

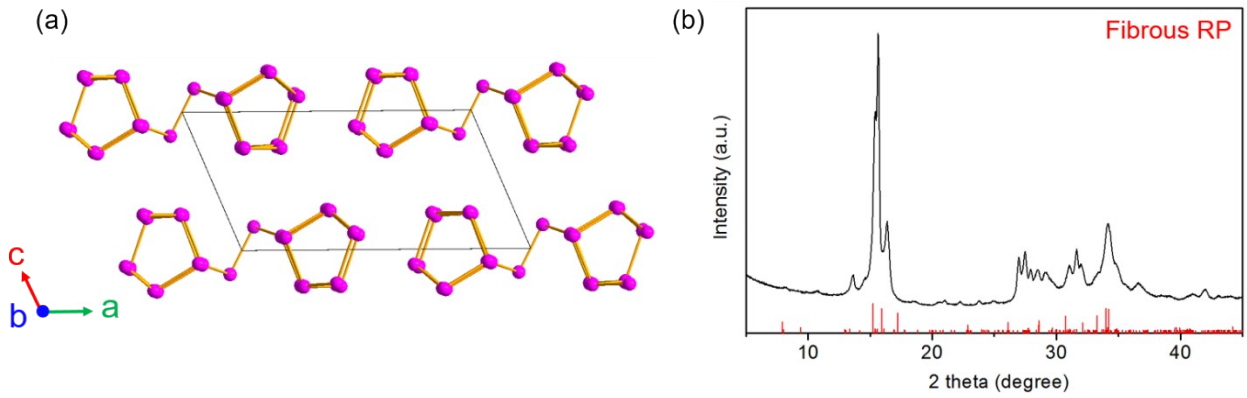

Figure S2. (a) Crystal structure and (b) simulated XRD pattern (red lines) of fibrous red phosphorus.[1] The black curve in (b) represents Form II RP.

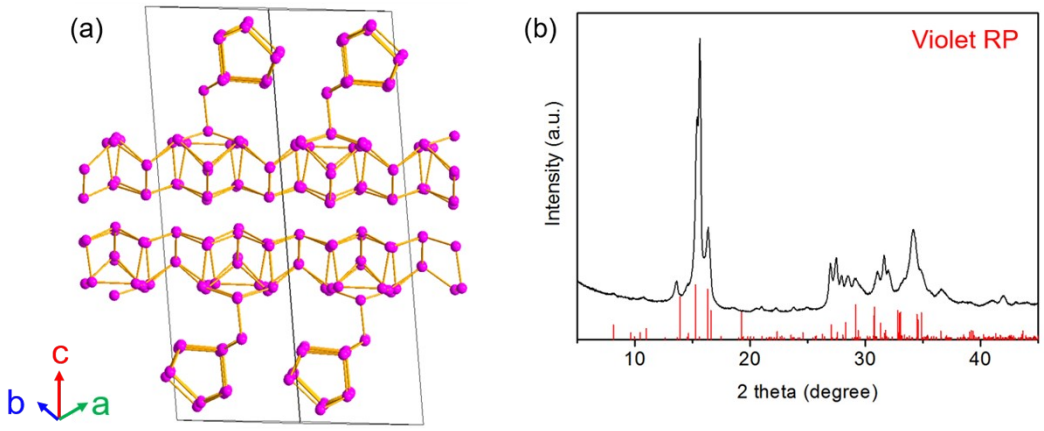

Figure S3. (a) Crystal structure and (b) simulated XRD pattern (red lines) of violet red phosphorus (Hittorf's Phosphorus).[2] The black curve in (b) represents Form II RP.

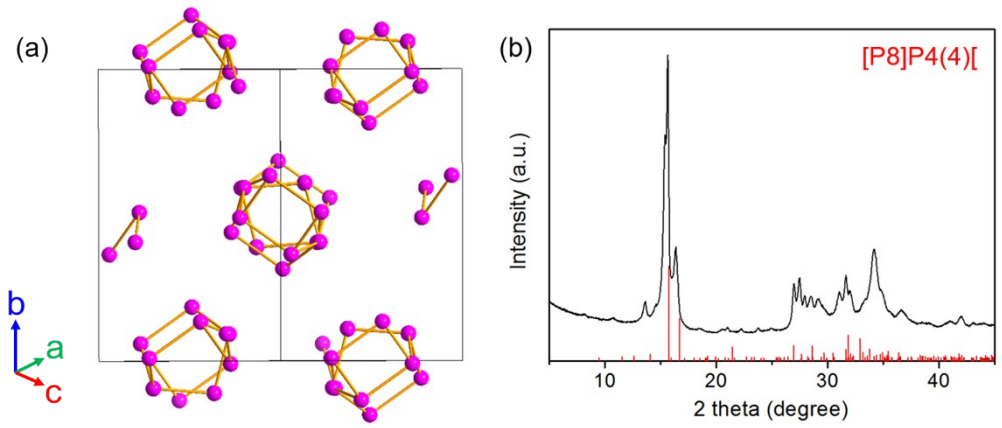

Figure S4. (a) Crystal structure and (b) simulated XRD pattern (red lines) of [P8]P4(4)[.[3] The black curve in (b) represents the measured XRD pattern of the as-synthesized Form II RP.

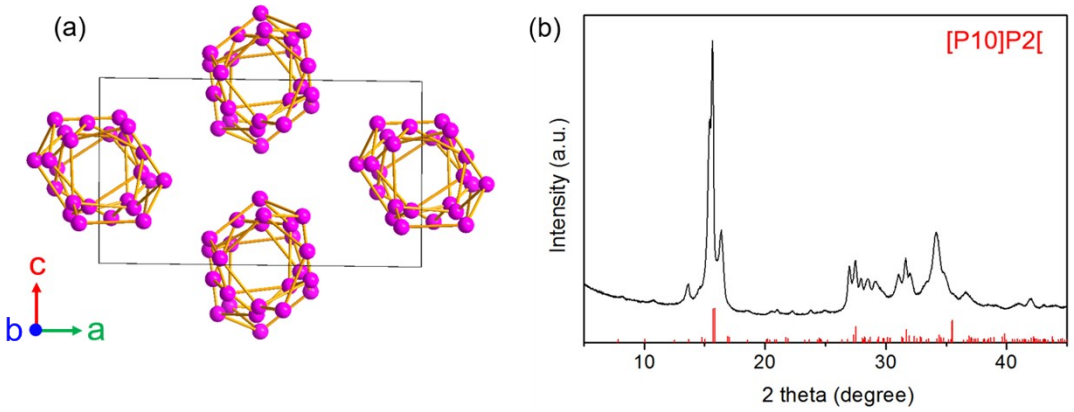

Figure S5. (a) Crystal structure and (b) simulated XRD pattern (red lines) of [P10]P2[.[3] The black curve in (b) represents Form II RP.

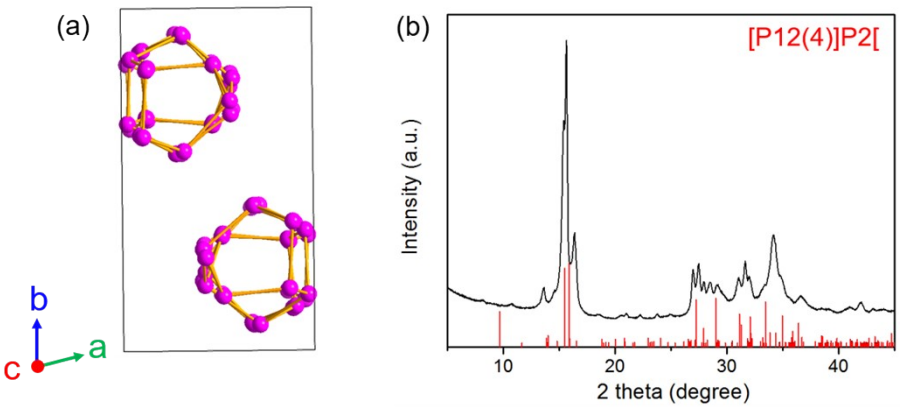

Figure S6. (a) Crystal structure and (b) simulated XRD pattern (red lines) of [P12(4)]P2[.[3] The black curve in (b) represents Form II RP.

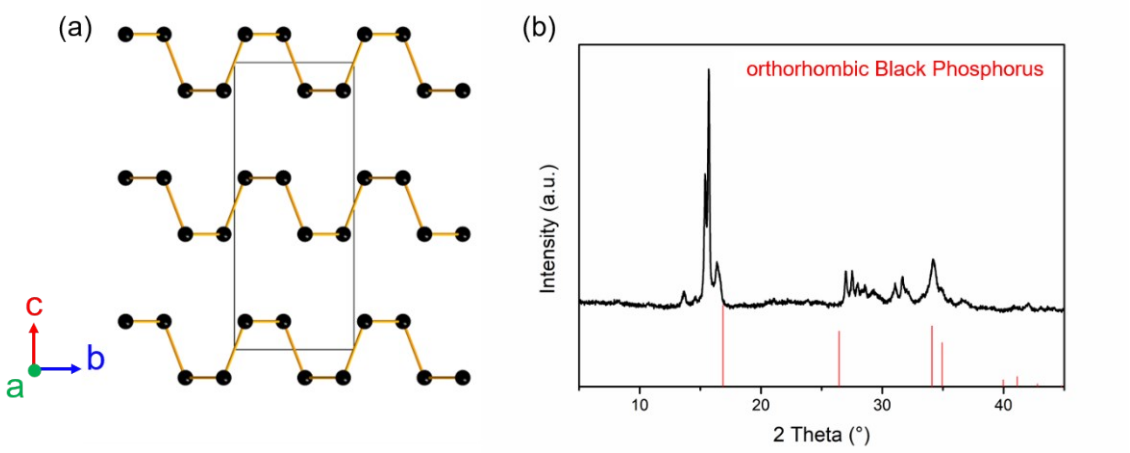

Figure S7. (a) Crystal structure and (b) simulated XRD pattern (red lines) of orthorhombic black phosphorus (a = 3.3200 Å, b=4.3900 Å, c=10.5200 Å).[4] The black curve in (b) represents Form II RP.

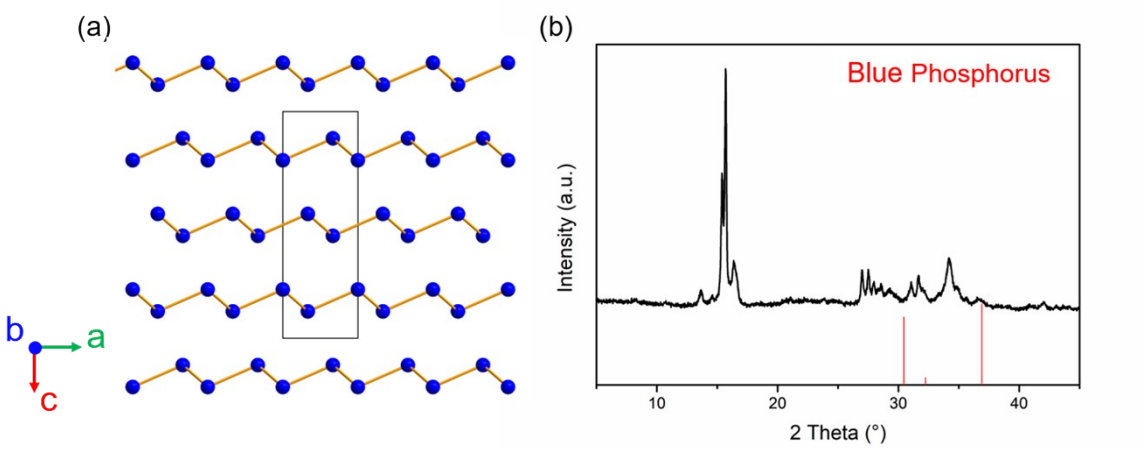

Figure S8. (a) Crystal structure and (b) simulated XRD pattern (red lines) of blue phosphorus.[5] The black curve in (b) represents Form II RP.

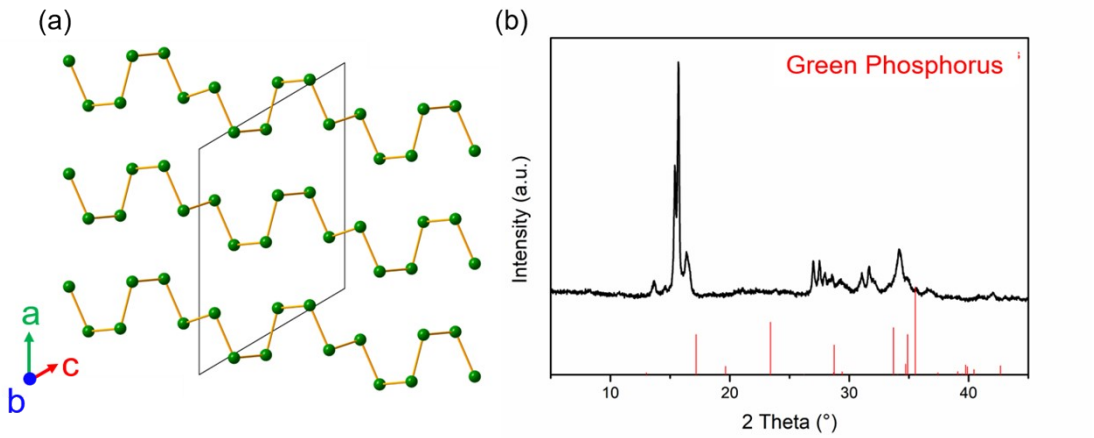

Figure S9. (a) Crystal structure and (b) simulated XRD pattern (red lines) of green phosphorus.[6] The black curve in (b) represents Form II RP.

Additionally, XRD patterns of Form II RP and greenish phosphorus[7] are compared as well. For greenish phosphorus, strong peaks with 2θ values of 28.9° and 30.3° and weak peaks with 2θ values of 22.6°, 23.7°, 35.4°, and 37.1° apparently do not match the pattern of Form II RP from both the perspective of peak intensity and position.

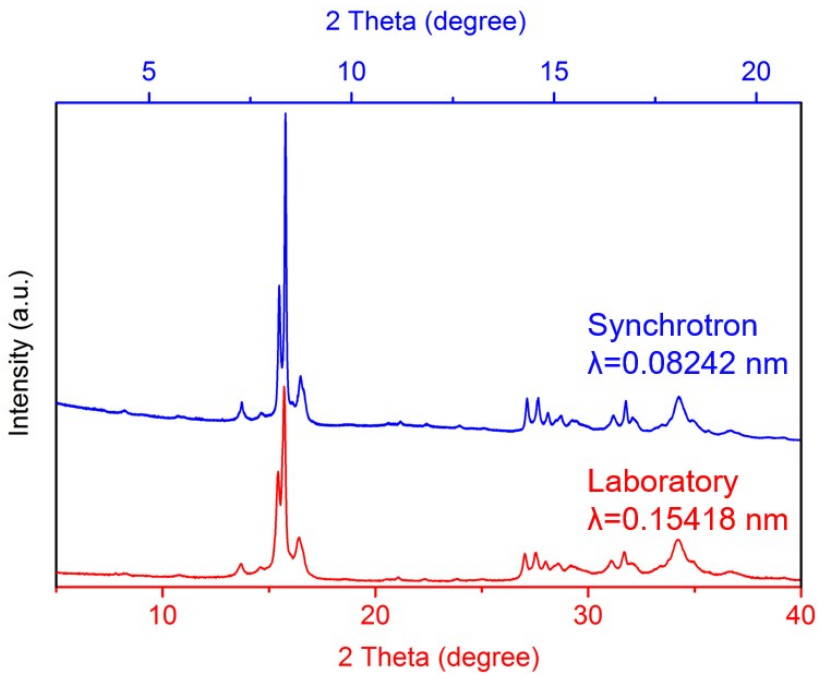

Figure S10. Stacked laboratory (LXRD) and synchrotron (SXRD) X-ray diffraction pattern for Form II RP.

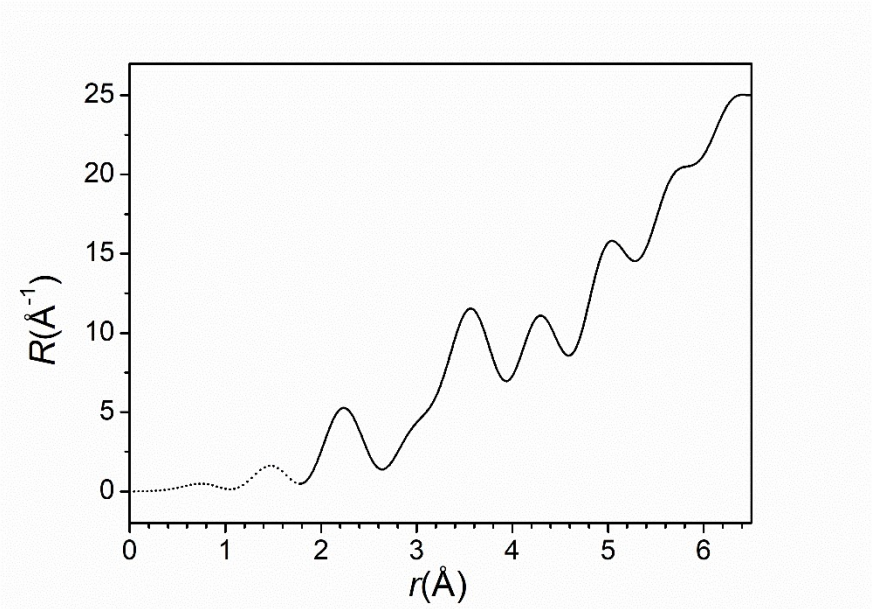

Figure S11. Radial distribution function (RDF) of Form II RP.

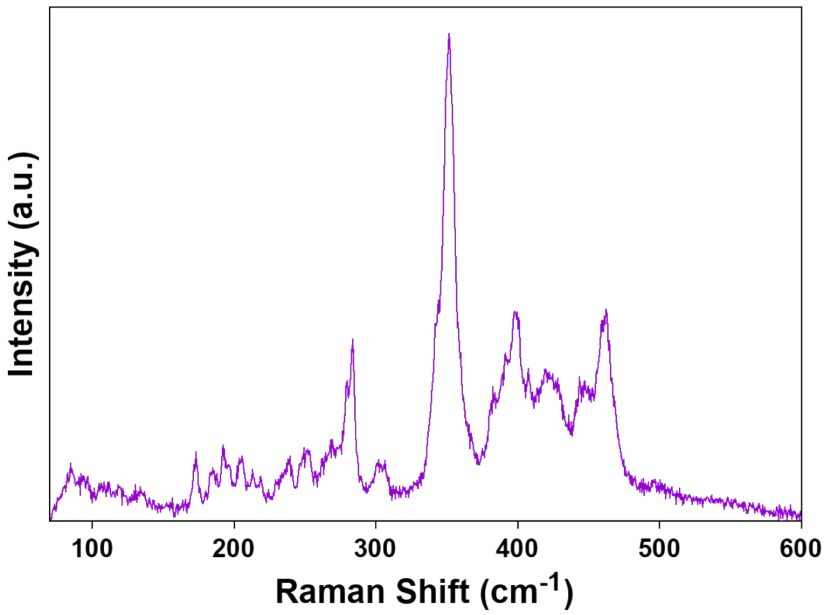

Figure S12. Raman spectra of Form II RP.

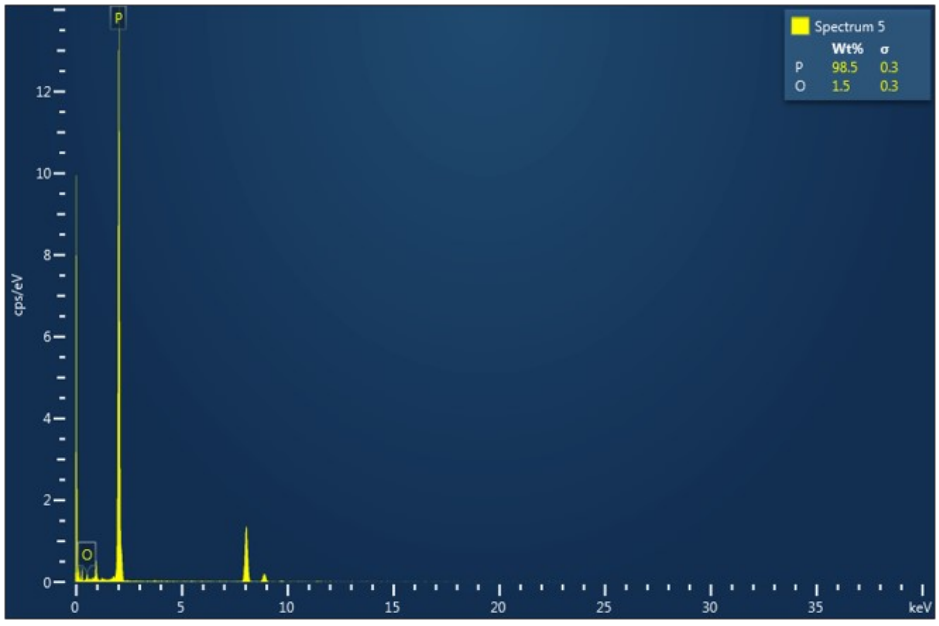

Figure S13. The representative EDS spectrum of Form II RP in Figure 2e. (Peaks located at 8.0 eV and 8.9 eV can be attributed to the Kα and Kβ characteristic X-ray emission lines of Cu grid.)

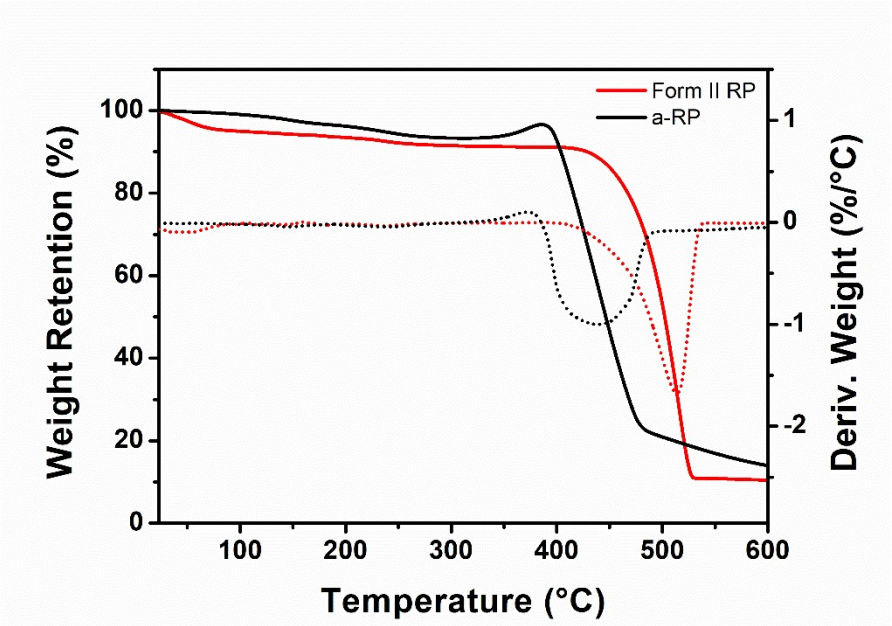

Figure S14. TG (solid line) / DTG (dotted line) plot of Form II RP and a-RP from room temperature to 600 °C.

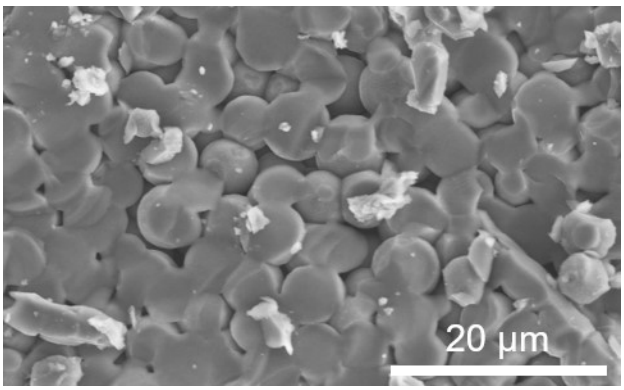

Figure S15. SEM image of the ground precursor a-RP. PL characterization was implemented on Form II RP products whose grain size is ~ 0.1 μm in diameter, while for a-RP the size is around 5~6 μm in characteristic length (Figure 2a).

Table S1. Fitting parameters of the TRPL decay curves of Form II RP.

Sample	A_1	τ_1 (ps)	A_2	τ_2 (ps)	τ_{av}* (ps)
Form II RP	1.430	5.440	0.005	296.6	52.07

* Note: The average photoluminescence lifetime was calculated by $\tau_{av} = \frac{\Sigma_i A_i \tau_i^2}{\Sigma_i A_i \tau_i}$.

References

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