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

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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.\textsuperscript{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).\textsuperscript{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 2\(\theta\) values of 28.9° and 30.3° and weak peaks with 2\(\theta\) 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_{av}^*$ (ps)</th>
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<tbody>
<tr>
<td>Form II RP</td>
<td>1.430</td>
<td>5.440</td>
<td>0.005</td>
<td>296.6</td>
<td>52.07</td>
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* Note: The average photoluminescence lifetime was calculated by $\tau_{av} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}$.

References


