

Article

# Growth and Characterization of Tetraphenylphosphonium Bromide Crystal

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**Abstract:** Multiple-phenyl phosphorous compounds are a group of chemical materials that have been used as reactants, pharmaceutical intermediates, extractants, and catalysts in organic synthetic reactions. However, the crystal growth of bulk crystals of multiple-phenyl phosphorous compounds, which may expand their applications in photonics technology, have been largely overlooked. In this article, the crystal growth of tetraphenylphosphonium bromide (TPPB) has been studied in organic solvents and water. The crystal structures and crystallization features are analyzed by X-ray diffraction data. By a slow temperature-lowering method, a single-crystal of TPPB ( $2\text{H}_2\text{O}$ ) with the size of  $27 \times 20 \times 20 \text{ mm}^3$  has been obtained in water. The basic thermal and optical properties were characterized. We find that the TPPB ( $2\text{H}_2\text{O}$ ) crystal shows excellent transparent property in the near-IR region. Large Raman shifts and strong Raman scattering intensity indicate that TPPB is a potential candidate in Raman-scattering-based nonlinearity applications.

**Keywords:** tetraphenylphosphonium bromide; single-crystal; crystal growth; transmission; Raman scattering

## 1. Introduction

Multiple-phenyl phosphorus-centered compounds such as triphenylphosphine oxide (TPPO) [1], triphenylphosphine sulfide (TPPS) [2], and phosphonium salts [3] are a class of tetrahedral-shaped molecules based on the  $sp^3$  hybridization of a phosphorous atom [4]. They have generated great interest because of their important applications in organic chemical fields. Over the years, multiple-phenyl phosphorus-centered compounds have been widely studied and utilized as active reactants [5–7], pharmaceutical intermediates [8], extractants [9], and catalysts [10–13] in organic syntheses. However, crystal growth of bulk multiple-phenyl phosphorus-centered crystals, which may expand the applications of this group of materials in photonics technology, has been overlooked.

As we know, most organic molecules possess a flexible backbone or a long branched chain, which generally exhibit poor crystallization habits. This is the very reason for why organic functional single-crystal materials are, at present, far less than inorganic candidates in practical use. However, multiple-phenyl phosphorus-centered compounds are characterized by rigid molecular structures in small-size and high symmetry, which have the possibility to grow into large-size crystal materials. Among such multiple-phenyl phosphorus-centered compounds, TPPO itself can not only form high quality crystals easily, but also can transform organic compounds bearing poor crystallization habits into useful large blocky crystals [14]. Moreover, TPPS can also act as a template to induce the crystallization of inorganic or organic compounds [7].

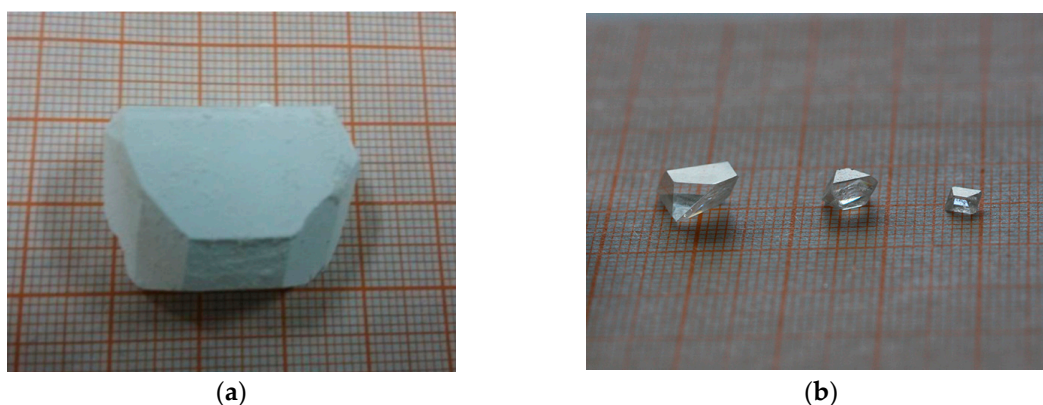
In this article, crystal growth of tetraphenylphosphonium bromide (TPPB) is studied in two different solvent systems of organic solvents and water. Compared to neutral compounds, multiple-phenyl phosphorus-centered salts have even better crystallization features due to the

Coulomb interaction between the tetraphenylphosphonium cation and anion. Large-size bulk single-crystals of TPPB were obtained in water by a temperature-lowering growth method in this work. The crystal structure was analyzed by X-ray diffraction. The thermal and optical properties were characterized. Raman scattering experiments show that single-crystal of TPPB is a potential functional material for Raman-scattering based nonlinearity applications such as Raman laser.

## 2. Results and Discussion

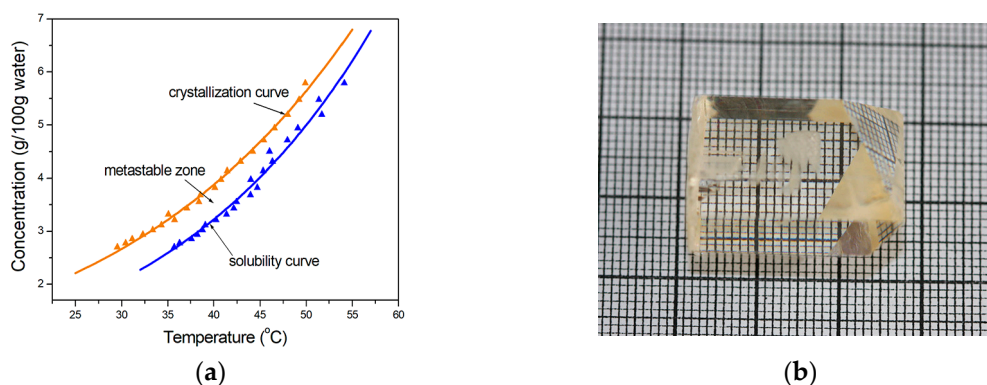
### 2.1. Crystal Growth

TPPB is an ionic organic compound which possesses excellent solubility not only in polar organic solvent, but also in water. In the experiment, we found that TPPB can grow into a large-size single-crystal in 3:2 mixture solvents of dichloromethane and n-hexane by spontaneous nucleation growth. However, the crystal became efflorescence rapidly under ambient conditions, although it exhibited high quality in the parent solution (Figure 1a). Spontaneous nucleation and growth of TPPB in ethanol and water were also studied. By slow evaporation of ethanol saturated solution, TPPB can crystallize into bulk transparent crystal. A small size TPPB single-crystal can also be obtained in saturated water solution by slow controlled cooling growth over a long period of time (Figure 1b).



**Figure 1.** (a) Efflorescent TPPB crystal grown by the evaporation of mixed 3:2 solvents of dichloromethane and n-hexane. The crystal has sharp edges and well-defined crystal faces, which indicates an excellent quality before efflorescence; (b) TPPB crystal obtained by spontaneous nucleation and growth in water.

The solubility and crystallization curve of TPPB in water were measured before the growth of a large-size TPPB crystal. The results are shown in Figure 2a. The triangles are the experimental data which were determined by the relationship of the temperature and turbidity using an automated crystallization screening system (see Materials and Methods). The solid lines are the fitting curves based on the measured data. The blue line is the solubility curve and the orange line is the crystallization curve. The metastable zone is between the solubility and crystallization curves. The average width of the metastable zone is about 5 °C. As shown in Figure 2a, the solubility of TPPB exhibits a rapid increase with the increased temperature. Accordingly, a temperature-lowering method was adopted for the growth of TPPB in water. The experiment adopted the top-seeded growth method. A high-quality seed was used. The temperature-controlling programme was set from 50 °C to 38 °C with the cooling speed of 0.24 °C/24 h. Figure 2b shows the single-crystal of TPPB obtained with a size of 27 mm × 20 mm × 20 mm. The crystal is transparent with a little inclusion. The transparent parts exhibit high optical quality. According to the comparison of TPPB crystals with other multiple-phenyl phosphorous crystals such as TPPS and coordination compounds of TPPO grown in our former work [15] (see also Supporting Information), TPPB is the best candidate possessing excellent crystal growth habits of large-size, high quality and easy growth.

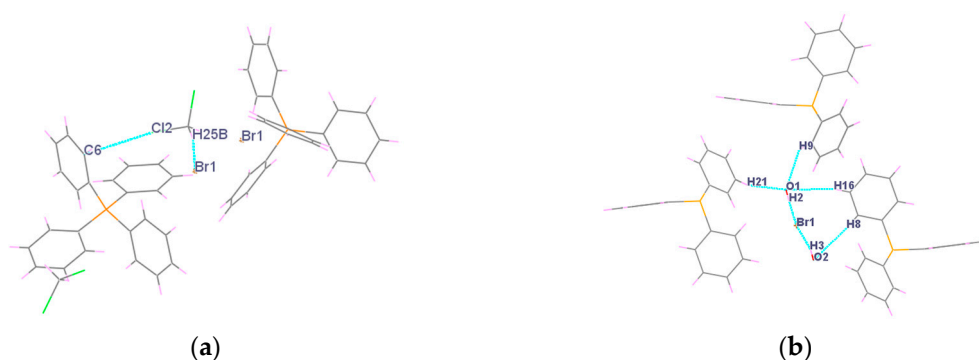


**Figure 2.** (a) TPPB solubility and crystallization curves in water. The triangles are the data measured. The solid curves are the fitted results based on the experimental data; (b) TPPB single-crystal with a size of 27 mm × 20 mm × 20 mm, grown by the temperature-lowering method.

## 2.2. X-ray Structural Analysis

The single-crystal structures of TPPB crystallized in the abovementioned different growth systems were analyzed by X-ray diffraction. The results showed that TPPB forms a dichloromethane solvated phase TPPB ( $\text{CH}_2\text{Cl}_2$ ) in mixed solvents of dichloromethane and n-hexane. The crystal structure belongs to the monoclinic system and the  $P2_1/n$  space group with  $a = 10.3525(14)$  Å,  $b = 16.925(2)$  Å,  $c = 13.4858(17)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 95.727(2)^\circ$ . The structure is as same as a previously reported dichloromethane-solvated TPPB crystal [16]. TPPB in water or ethanol forms the same dihydrate crystal TPPB ( $2\text{H}_2\text{O}$ ), which is an orthogonally system and  $Pnma$  space group with  $a = 16.2842(10)$  Å,  $b = 10.8087(10)$  Å,  $c = 12.6638(12)$  Å and  $\alpha = \beta = \gamma = 90^\circ$ , as previously reported [17]. The X-ray crystal structure data obtained in this work are summarized in the Supporting Information materials.

The short interaction of the solvent molecules with parent molecules in crystals of TPPB ( $\text{CH}_2\text{Cl}_2$ ) and TPPB ( $2\text{H}_2\text{O}$ ) were analyzed in order to explore the exact reason for the stability of the solvated TPPB crystals. The results are shown in Figure 3a,b and Table 1. Figure 3a shows that there are only two types of short contacts related to the solvent molecule in the TPPB ( $\text{CH}_2\text{Cl}_2$ ) crystal. Dichloromethane interacts weakly with the phenyl ring of TPPB by  $\text{Br}1 \dots \text{H}25\text{B}$  and  $\text{C}6 \dots \text{Cl}2$ . By contrast, six types of short interactions exist in between TPPB and water molecules. Among them, oxygen in two water molecules forms four  $\text{O} \dots \text{H}$  short distance interactions to the surrounding carbon atom of TPPB molecules. In addition, hydrogen atoms of two water molecules have short contacts with Br ions, respectively. As shown in Table 1, the  $\text{Br} \dots \text{H}$  interaction in TPPB ( $\text{CH}_2\text{Cl}_2$ ) is weaker than that in TPPB ( $2\text{H}_2\text{O}$ ) due to the longer contact distance. Therefore, the weak intermolecular interaction of the dichloromethane molecule with the parent TPPB molecule is the very reason for the rapid efflorescence of TPPB ( $\text{CH}_2\text{Cl}_2$ ). By contrast, TPPB ( $2\text{H}_2\text{O}$ ) can keep stable under the same ambient conditions.



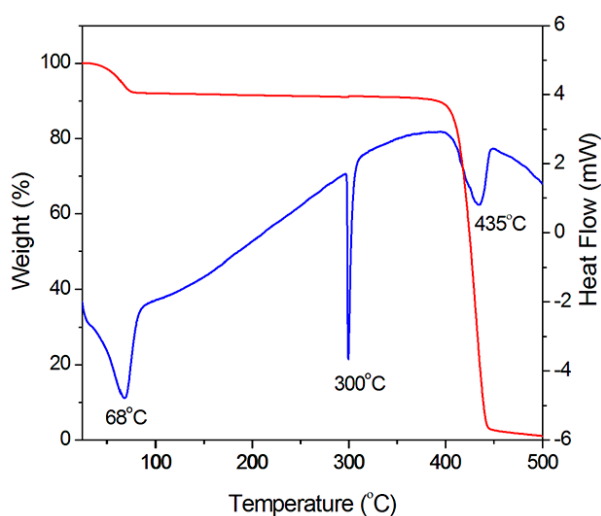
**Figure 3.** Short contacts between solvent and parent molecules in (a) TPPB ( $\text{CH}_2\text{Cl}_2$ ); (b) TPPB ( $2\text{H}_2\text{O}$ ).

**Table 1.** Intermolecular contacts of TPPB to the solvent molecules shorter than the sum of the van der Waals (vdW) radii in the solvated crystals.

TPPB (CH <sub>2</sub> Cl <sub>2</sub> )		TPPB (2H <sub>2</sub> O)	
Symmetry codes: <sup>I</sup> x, y, z; <sup>II</sup> - 1/2 + x, 1.5 - y, 1/2 + z		Symmetry codes: <sup>I</sup> x, y, x; <sup>II</sup> 1/2 + x, 1.5 - y, 1/2 - z; <sup>III</sup> 1/2 + x, 1/2 - y, 1/2 - z; <sup>IV</sup> 1/2 - x, 1 - y, - 1/2 + z; <sup>V</sup> 1 - x, 1/2 + y, 1 - z	
<sup>I</sup> Br1... <sup>II</sup> H25B	2.772	<sup>I</sup> Br1... <sup>II</sup> H3	2.454
<sup>I</sup> C6... <sup>II</sup> Cl2	3.354	<sup>I</sup> Br1... <sup>III</sup> H2	2.447
		<sup>I</sup> H9... <sup>I</sup> O1	2.692
		<sup>IV</sup> H8... <sup>I</sup> O2	2.641
		<sup>IV</sup> H21... <sup>I</sup> O1	2.677
		<sup>IV</sup> H16... <sup>V</sup> O1	2.699

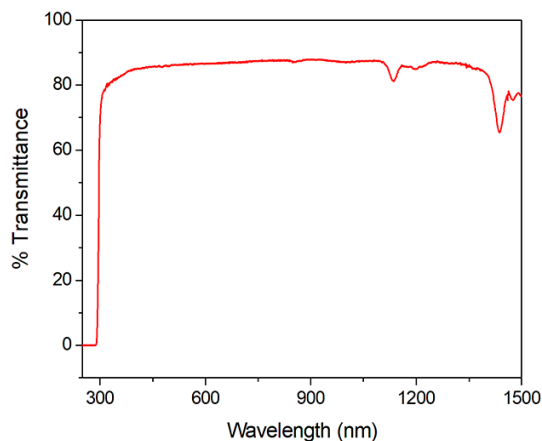
### 2.3. Thermal Property

The thermal property of TPPB (2H<sub>2</sub>O) was studied. The thermogravimetry analysis (TGA) curve in Figure 4 shows that there is a weight loss of 8.8% at 68 °C, which is attributed to the loss of two water molecules as the temperature increases. In the differential scanning calorimetry (DSC) curve, the water loss corresponds to an endothermic process at 68 °C. The melting point of TPPB (2H<sub>2</sub>O) is 300 °C and the decomposition point is 435 °C. TPPB has a relative high decomposition temperature compared to general organic compounds.

**Figure 4.** TG-DTA curves of TPPB (2H<sub>2</sub>O).

### 2.4. Optical Transmission Spectrum

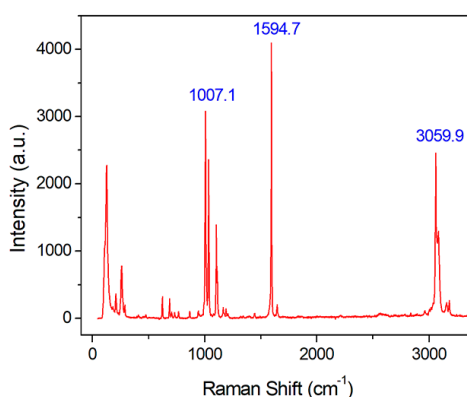
The optical transmission spectrum of the TPPB (2H<sub>2</sub>O) single-crystal with a thickness of 0.5 mm is shown in Figure 5. The crystal exhibits excellent transmission from 300 nm to 1350 nm. The weak peaks at 1136 nm and 1437 nm are attributed to the vibrational absorption of water molecules in the crystal lattice [18]. Anhydrous TPPB crystals are expected to decrease or even eliminate the absorption of water in the near-IR region.



**Figure 5.** Transmission spectrum of the TPPB (2H<sub>2</sub>O) single-crystal with a thickness of 0.5 mm.

### 2.5. Raman Scattering Property

The Raman scattering spectrum of TPPB (2H<sub>2</sub>O) was measured by the excitation of a 473 nm laser using a confocal LabRAM HR800 Raman spectrometer (Figure 6). There are three strong peaks with Raman shifts over 1000 cm<sup>-1</sup> at 3059.9 cm<sup>-1</sup>, 1594.7 cm<sup>-1</sup>, and 1007.1 cm<sup>-1</sup>, respectively. Since the C-H stretching vibrations in the single-substitutional benzene ring are dominant in vibration modes of TPPB, the peak located at 3059.9 cm<sup>-1</sup> is strong [19]. The peak at 1594.7 cm<sup>-1</sup> is attributed to the stretching vibration of the benzene ring. Also, the strong peak at 1007.1 cm<sup>-1</sup> is the other Raman characteristic line of the single-substitutional benzene ring of TPPB. In this experiment, we also explored the Raman scattering spectra of a series of multiple-phenyl substituted compounds involving triphenylphosphine, triphenylphosphine oxide, triphenylphosphine sulfide, coordination compound of triphenylphosphine oxide, and sodium tetraphenylboron (see Supporting Information). We found that the main Raman shifts are similar in these compounds and in fact insusceptible to the number of the phenyl group, element in tetrahedron center, ligands, or the type of the crystal, e.g., molecular crystal or ionic crystal. Accordingly, and considering the high quality of the crystal and strong Raman scattering properties, TPPB (2H<sub>2</sub>O) crystal can be used as a potential material in Raman scattering-related nonlinear research and applications.



**Figure 6.** Raman scattering spectrum of the TPPB (2H<sub>2</sub>O) single-crystal excited by a 473 nm laser.

## 3. Materials and Methods

### 3.1. Reagents

Tetraphenylphosphonium bromide (99%) and organic solvents used (HPLC grade) were purchased from J&K Scientific Ltd.

### 3.2. Solubility and Crystallization Curves

The solubility and crystallization curves were measured using the CrystalSCAN Automated Crystallisation Screening System (HEL). The curves were determined by the relationship of the temperature and turbidity of the solution. In the experiment, 2.0262 g TPPB was added to 35 mL Milli-Q water in the reactor and heated. When the solution became clear and the crystals dissolved, the solution continued to be heated to 70 °C and was kept for 30 min. Then, the solution was cooled down at a speed of 0.5 °C/min until the solution became turbid. The turbidity probe was used to record the two temperatures at the points when the solution became clear and the crystals reappeared. Twenty-one cycles were measured in the experiments. The resulting data of solubility were fitted based on an exponential growth function  $y = 0.56234e^{(x/22.89889)}$ . The goodness of fit was 0.98092. The crystallization data were fitted by the exponential growth function  $y = 0.86949e^{(x/26.762)}$ . The corresponding goodness of fit was 0.99509.

### 3.3. Single-Crystal X-ray Diffraction

Single crystal XRD was carried out on a Bruker SMART APEX-II diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal data were collected at room temperature (296 K). The molecular structures and packing arrangements were obtained by direct computation methods and then refined by the full-matrix least-squares technique on  $F^2$  using the SHELX algorithm [20]. The summary of the crystal structure data are shown in Supporting Information.

### 3.4. Thermal and Optical Transmission Measurement

Differential scanning calorimetry and thermogravimetry analysis (DSC/TGA) were carried out using a Mettler-Toledo TGA/DSC1/1600HT Thermal Analyzer. The temperature ranged from room temperature to 500 °C with the heating rate of 5 °C/min. The sample was placed in an Al<sub>2</sub>O<sub>3</sub> crucible with Ar gas flowing at a rate of 60 mL/min to avoid oxidation at high temperatures. The transmission spectra were measured on a Hitachi U-3500 spectrophotometer.

### 3.5. Raman Scattering Spectrum

The Raman scattering spectrum of the TPPB single-crystal was measured on a confocal LabRAM HR800 Raman spectrometer (Horiba JY). The wavelength of the excitation laser was 473 nm with the laser power of 20 mW. A 50  $\times$  microscope was used during the collection of the data. The exposure time was 10 s.

## 4. Conclusions

In summary, the crystal growth of TPPB has been studied in different solvent systems. Our experiment showed that TPPB has excellent crystallization habits of growing into large-size and high quality crystals in water. The water-solvated TPPB crystal exhibited a high transmission ratio from visible to near-IR regions. The strong Raman scattering over 1000 cm<sup>-1</sup> indicates that TPPB crystals can be employed in Raman scattering-related nonlinear applications such as Raman lasers.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4352/7/6/154/s1](http://www.mdpi.com/2073-4352/7/6/154/s1), Figure S1: The bulk crystal of TPPS grown in our group, Table S1: Crystallographic data and refinement details of TPPB obtained in this work and reported in literature.

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**Author Contributions:** Yan Ren and Xutang Tao conceived and designed the experiments; Guangqiang Wang and Xiaolong Liu performed the experiments; Yan Ren and Chengqian Zhang analyzed the data; Yan Ren wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Bandoli, G.; Bortolozzo, G.; Clemente, D.A.; Croatto, U.; Panattoni, C. Crystal and molecular structure of triphenylphosphine oxide. *J. Chem. Soc. A* **1970**, 2778–2780. [CrossRef]
2. Coddling, P.W.; Kerr, K.A. Triphenylphosphine sulfide. *Acta Crystallogr. B* **1978**, B34, 3785–3787. [CrossRef]
3. Burgess, K.M.N.; Korobkov, I.; Bryce, D.L. A combined solid-state NMR and X-ray crystallography study of the bromide ion environments in triphenylphosphonium bromides. *Chem. Eur. J.* **2012**, 18, 5748–5758. [CrossRef] [PubMed]
4. Corbridge, D.E.C. *Phosphorous: An Outline of Its Chemistry, Biochemistry and Technology*, 5th ed.; Elsevier: Amsterdam, The Netherlands, 1980; ISBN 0444893075.
5. Chu, T.; Vyboishchikov, S.F.; Gabidullin, B.; Nikonov, G.I. Oxidative cleavage of C=S and P=S bonds at an All center: Preparation of terminally bound aluminum sulfides. *Angew. Chem. Int. Edit.* **2016**, 55, 13306–13311. [CrossRef] [PubMed]
6. O'Brien, C.J.; Lavigne, F.; Coyle, E.E.; Holohan, A.J.; Doonan, B.J. Breaking the ring through a room temperature catalytic Wittig reaction. *Chem. Eur. J.* **2013**, 19, 5854–5858. [CrossRef] [PubMed]
7. Djordjevic, B.; Schuster, O.; Schmidbaur, H. A cyclic hexamer of silver trifluoroacetate supported by for triphenylphosphine sulfide template molecules. *Inorg. Chem.* **2005**, 44, 673–676. [CrossRef] [PubMed]
8. Kozminykh, V.O.; Igidov, N.M.; Kozminykh, E.N.; Aliev, Z.G. Reactions of 5-aryl-furan-2,3-diones with acylmethylenetriphenylphosphoranes-synthesis and biological-activity of 3(2H)-furanone derivatives. *Pharmazie* **1993**, 48, 99–106. [PubMed]
9. El-Shahawi, M.S.; Hassan, S.S.M.; Othman, A.M.; Zyada, M.A.; El-Sonbati, M.A. Chemical speciation of chromium(III,VI) employing extractive spectrophotometry and tetraphenylarsonium chloride or tetraphenylphosphonium bromide as ion-pair reagent. *Anal. Chim. Acta* **2005**, 534, 319–326. [CrossRef]
10. Varma, R.S.; Naicker, K.P.; Liesen, P.J. Palladium chloride and tetraphenylphosphonium bromide intercalated clay as a new catalyst for the Heck reaction. *Tetrahedron Lett.* **1999**, 40, 2075–2078. [CrossRef]
11. Suzuki, H.; Kageyama, H.; Yoshida, Y.; Kimura, Y. Tetraphenylphosphonium bromide-catalyzed 'Halex' fluorination of chloroaryl sulfonyl chlorides. *J. Fluor. Chem.* **1991**, 55, 335. [CrossRef]
12. Han, J.; Wu, H.; Teng, M.Y.; Li, Z.Y.; Wang, Y.N.; Wang, L.Y.; Pan, Y. Novel tripod L-prolinamide catalysts based on tribenzyl- and triphenylphosphine oxide for the direct aldo reaction. *Syn. Lett.* **2009**, 6, 933–936. [CrossRef]
13. Kim, S.S.; Lee, S.H. Asymmetric cyanohydrin synthesis catalyzed by Mn(salen) complex/triphenylphosphine oxide. *Syn. Commun.* **2005**, 35, 751–759. [CrossRef]
14. Etter, M.C.; Baures, P.W. Triphenylphosphine oxide as a crystallization aid. *J. Am. Chem. Soc.* **1988**, 110, 639–640. [CrossRef]
15. Liu, X.L.; Wang, G.Q.; Dang, Y.Y.; Zhang, S.J.; Tian, H.L.; Ren, Y.; Tao, X.T. A new potential nonlinear optical hybrid semiorganic crystal of ZnMnCl<sub>4</sub>(TPPO)<sub>4</sub> with attractive physical properties. *CrystEngComm* **2016**, 18, 1818–1824. [CrossRef]
16. See the Crystal Structural Data Deposited in Cambridge Crystallographic Data Center with the CCDC Number 270973. Available online: <http://webofsd.ccdc.cam.ac.uk> (accessed on 15 March 2017).
17. Vincent, B.R.; Knop, O.; Linden, A.; Stanley Cameron, T.; Robertson, K.N. Crystal chemistry of tetra-radial species. Part 2. Crystal structures of Et<sub>4</sub>Ni, Ph<sub>4</sub>PBr·H<sub>2</sub>O, and Ph<sub>4</sub>PBr·2H<sub>2</sub>O. *Can. J. Chem.* **1988**, 66, 3060–3069. [CrossRef]
18. Curcio, J.A.; Petty, C.C. The near infrared absorption spectrum of liquid water. *J. Opt. Soc. Am.* **1951**, 41, 302–304. [CrossRef]
19. Dollish, F.R.; Fateley, W.G.; Bentley, F.F. *Characteristic Raman Frequencies of Organic Compounds*; Wiley-Interscience: New York, NY, USA, 1974; ISBN 0471217697.
20. Sheldrick, G.M. A short history of SHELX. *Acta Cryst.* **2008**, A64, 112–122. [CrossRef] [PubMed]

