# Triboluminescence and Vapor-Induced Phase Transitions in the Solids of Methyltriphenylphosphonium Tetrahalomanganate(II) Complexes

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Ⓢ Supporting Information

ABSTRACT: Triboluminescence (TL) of the methyltriphenylphosphonium tetrahalomanganate(II) complexes such as bis(methyltriphenylphosphonium) tetrabromomanganate (**PMBB**) and bis(methyltriphenylphosphonium) dibromodichloromanganate (**PMBC**) was switched ON and OFF reversibly by vapors of aprotic and protic solvents, respectively, for the first time. Detailed analyses indicate that solids of the **PMBB** and the **PMBC** undergo phase transitions depending on the environment, which regulate the TL activity of these compounds. The combined results of luminescence, powder X-ray diffraction, differential scanning calorimetry, and electron paramagnetic resonance were used to demonstrate crystal dynamism as well as the TL emission of **PMBB** and **PMBC**.
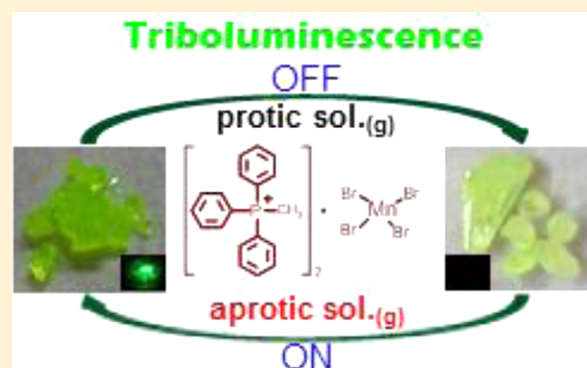
INTRODUCTION

Triboluminescence[1] (TL), also known as mechanoluminescence or fractoluminescence, is light emission resulting from mechanical action on a solid. This phenomenon has been observed in several organic[2] and inorganic solids[2] and their complexes.[1,2] However, often TL materials lose their luminescent property, either partially or completely, by experimental and environmental influences; therefore, their practical applications have not been extensively studied.[1−3] Analyses on the effect of varying temperature,[4a] pressure,[4b] dopants,[4c] impurities,[5] etc.,[4,5] on the luminescence have been documented. However, since TL occurs in solids, understanding about the structure−activity[2] as well as crystal dynamics[6] relationships and their controls are essential.[1]

Chandra and Zink[7] have reported on the correlation between the crystal structure and the TL emission of different sets of solids. They concluded that the piezoelectric properties of noncentrosymmetric crystals are the source of TL. Nevertheless, several centrosymmetric structures of terbium(III) complexes,[8] europium(III) complexes,[9] alkali halides,[10] and glassy polymers[11] have been reported to be TL active. Thus, other factors are involved in the functional attributes of solids in addition to the structure−property relationship.[1,2]

The molecular dynamism[6b] in the three-dimensional lattices has been demonstrated to affect the physical,[12] chemical,[13] and biological[14] properties of the solid substances. For example, nonluminescent Au(I) complexes[15] of $[Au(S_2CN(C_5H_{11})_2)]_2$ series displayed luminescence when they were exposed to acetone, dichloromethane, and chloroform vapors. This is because the intermolecular interactions between the solvent

vapors and the complex twine the Au⋯Au distances[15a,f] in crystals. Likewise, the humidity-induced[12,16] structural dynamism has been described to accelerate the rate of multicomponent reactions in the condensed phase. Curiously, relations between the TL emission and the phase transformations have remain unexplored, maybe due to poor understanding of the theories involved.[1,2] Thus, the research concerning cause of phase transitions and their influences on the functional behaviors of solids under different experimental conditions is crucial,[4−6] since it may provide fundamental information to establish the suitable conditions at which the desired structures are most stable to acquire unique responses.[17]

Tetrahedrally coordinated manganese(II) complexes[18] constitute a special interest as they can be obtained easily by simple synthetic methods, as well as display interesting solid-state properties and have connections with technologically important phosphor materials. We chose the following Mn(II) complexes of bis(methyltriphenylphosphonium) tetrabromomanganate (**PMBB**, Chart 1) and the bis(methyltriphenylphosphonium) dibromodichloromanganate (**PMBC**, Chart 1) for the present investigations. Their synthesis, the characterizations, the reversible structural dynamism, as well as emissions of **PMBB** and **PMBC** are disclosed herein. To the best of our knowledge, how phase transformations in the solid form influence TL behavior has not been heretofore investigated.[1,2]

Chart 1. Molecular Structures of PMBB and PMBC

PMBB   PMBC
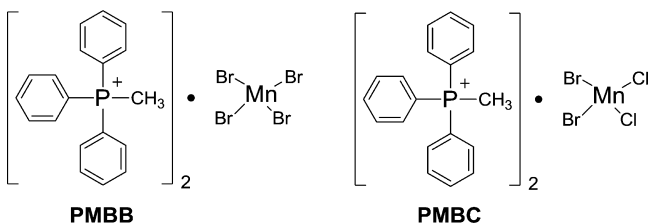
■ RESULTS AND DISCUSSION

Synthesis. **PMBB** and **PMBC** were obtained simply by mixing the methyltriphenylphosphonium bromide with $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$, respectively, in dry acetone at 80 °C, cf. Experimental Section. The stoichiometry and the purity of synthesized materials were confirmed by elemental analysis, IR, and NMR measurements. Large bright green crystals of **PMBB** and **PMBC**, obtained after 36−48 h of reaction, were found to be stable for several months in dry conditions. However, the bright green color of the crystals faded when exposed to atmospheric moisture at room temperature. Thus, the measurements were carried out under moisture-free conditions unless stated otherwise.

Luminescence Properties. Since **PMBB** and **PMBC** are ionic compounds, we anticipated that cleavage along the charged plane may provide the TL emission. The TL of these compounds (Chart 1) was tested by grinding the solids with a glass rod or with a custom-built drop tower. Surprisingly, newly grown crystals of **PMBB** and **PMBC** emitted a very strong green light (Figure 1), at room temperature, under both
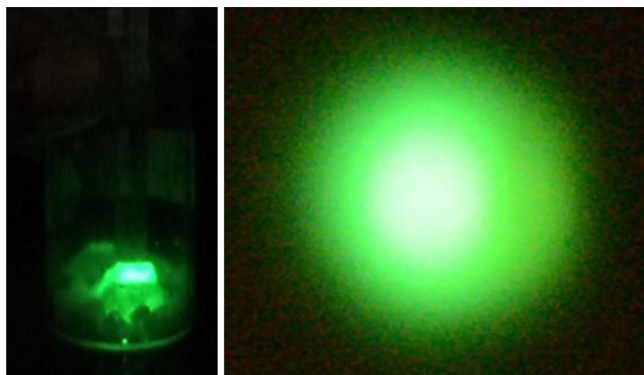
experimental conditions. Indeed, the TL of **PMBB** and **PMBC** was clearly seen in daylight and continued while the crystals were being crushed. We estimated the relative intensity of the light emitted from the crystals of **PMBB** and **PMBC**, upon grinding, by comparison with the emission of familiar manganese doped zinc sulfide (ZnS/Mn) and salicylsalicylic acid produced under identical conditions. The emission of **PMBB** and **PMBC** was found to be slightly weaker than that of the ZnS/Mn and stronger than that of the salicylsalicylic acid, cf. Supporting Information, Figure S1. A comparable TL emission intensity of **PMBB** and **PMBC** suggests that the effective charge recombination[19] occurs among the charged species of organic and inorganic units upon grinding.

The most brightly TL emissive materials are known to exhibit photoluminescence (PL) as well.[2] Therefore, **PMBB** and **PMBC** were irradiated ($\lambda = 365$ nm) with a hand-held UV lamp. Without any surprise they showed a bright green light (Figure 2), which is identical to their TL light (Figure 1). Thus, we presume that the PL and the TL emissions of **PMBB** and **PMBC** may originate from the same excited state.[20]

Effect of Solvent Vapors. We observed that the crystals of **PMBB** and **PMBC** lost their appearance and the TL emission, entirely, after approximately 30 d after synthesis, presumably due to the environmental influence.[16,20] Thus, the crystals of **PMBB** and **PMBC** from the same batch were divided into multiple portions and exposed to vapors of different solvents under controlled conditions. As expected, the color of the crystals changed from bright green to light green (Figure 3),
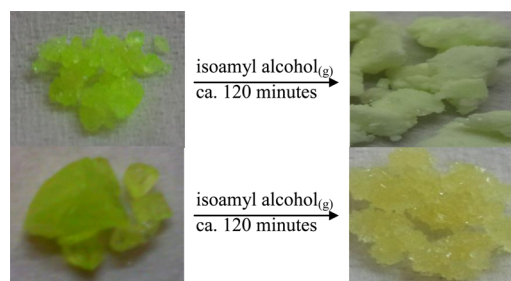
Figure 3. Photographs of the solids of **PMBB** (top) and **PMBC** (bottom), before and after exposure (ca. 120 min) to vapors of the isoamyl alcohol. Notice the color change by the effect of vapors of the isoamyl alcohol.

and the TL intensity was found to be reduced upon exposure (120−150 min) to protic solvents such as methanol, ethanol, isoamyl alcohol, and water. In contrast, similar exposure to vapors of aprotic solvents such as acetone and monoglyme affected neither the color nor the TL emission of the solids of
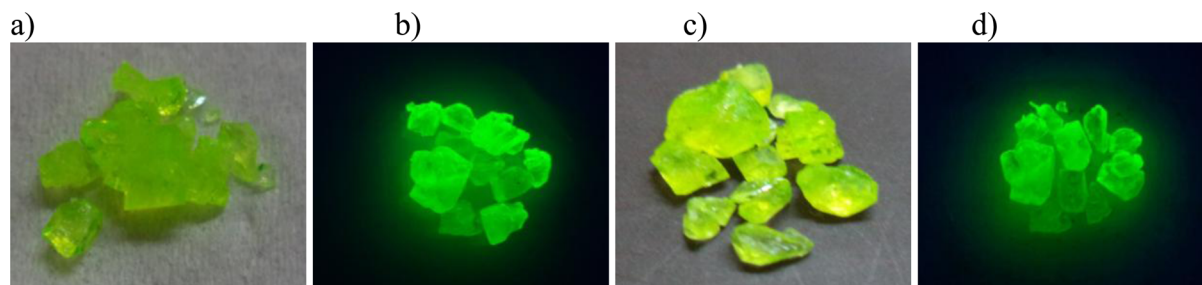

Figure 1. Photographs of the TL light captured from crystals of **PMBB** upon grinding with a glass rod (left) and a drop tower (right) at ambient conditions. The TL emission of **PMBC** was similar to that of **PMBB** and, thus, is not shown here.

Figure 2. Photographs of crystals of **PMBB** (a, b) and **PMBC** (c, d) under ambient light (a, c) and under UV light ($\lambda = 365$ nm) (b, d) obtained at room temperature.

PMBB and **PMBC**. In addition, the melting points of the crystals of **PMBB** and **PMBC** exposed to the vapors of aprotic solvents were not affected, whereas the crystals exposed into protic solvents melted at lower (<12−15 °C) temperature than that of freshly prepared complexes (**PMBB**; mp = 174−178 °C and **PMBC**; mp = 128−131 °C). These combined results clearly indicated that both **PMBB** and **PMBC** underwent phase transitions[6] when exposed to vapors of the protic solvents. This was further confirmed by powder X-ray diffraction (PXRD) analyses as well, vide infra.

We monitored the effects of vapors of the isoamyl alcohol on the crystals of **PMBB** and **PMBC** by PXRD analysis at different time intervals, cf. Figure 4 and Supporting Information, Figure
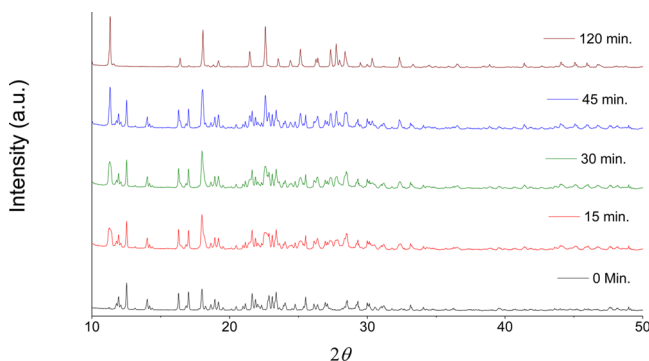
Figure 4. PXRD patterns of **PMBB** upon exposure to vapors of isoamyl alcohol at different time intervals (0−120 min). Notice the significant changes in the peak position and the intensity. An analogous figure for **PMBC** has been provided in Supporting Information, Figure S2.

S2. We observed that the PXRD patterns of both **PMBB** and **PMBC** changed gradually upon exposure to the isoamyl alcohol vapors, which was complete by 120 min. To evaluate the completeness of the phase transformations, the PXRD patterns of **PMBB** and **PMBC** obtained after 120 min of exposure to vapors of the isoamyl alcohol were compared with PXRD patterns of corresponding complexes obtained from isoamyl alcohol medium as a solvent of the synthesis. Indeed, PXRD patterns from both experiments are similar (Supporting Information, Figures S3 and S4), suggesting that **PMBB** and **PMBC** underwent the phase transition from one form to another form in a quantitative manner mediated by the protic solvent vapor. In other words, the crystal structrues of **PMBB** and **PMBC** are dynamically labile to the surroundings. In the ^{1}H NMR spectra (Supporting Information, Figure S5) of **PMBB** and **PMBC** exposed to isoamyl alcohol vapors for 2 h, the solvent molecules were hardly detected. In addition, IR spectra (Supporting Information, Figures S6 and S7) measured for the complexes exposed to the solvent vapors did not show any new peaks, suggesting that the solvent molecules are not included in the lattice. Thus, the structural transformations of **PMBB** and **PMBC** were triggered by exposure to the vapors, but the inclusion of vapor into the solid did not occur. Similar behaviors have been reported for several Pt(II) complexes[21] and Au(II) complexes.[15] In these instances the intermolecular interactions played a vital role in the structural dynamics.

To investigate whether the phase transitions are reversible, solids of **PMBB** were exposed to vapors of protic solvent (isoamyl alcohol) and aprotic solvent (acetone) alternatively and monitored by PXRD measurements. As shown in Figure 5,
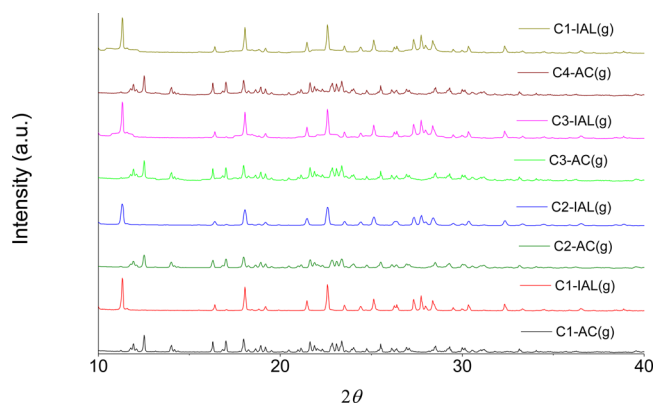

Figure 5. Changes in the PXRD patterns of **PMBB** as a function of exposure to acetone (90−120 min) and the isoamyl alcohol (120−130 min) solvent vapors. C indicates number of cycles; AC, acetone; IAL, isoamyl alcohol; g, gas.

when samples were exposed to vapors of isoamyl alcohol, new peaks appeared at $2\theta = 11.4°$ and 27.7°, and peaks at $2\theta = 12.6°$, 17.1°, and 24.4° disappeared simultaneously. In contrast, when the solid was exposed to acetone vapors, the peaks at $2\theta = 12.6°$, 17.1°, and 24.4° regained, and those at $2\theta = 11.4°$ and 27.7° vanished. Further, we observed repeated color change between the bright green to the light green and vice versa during the PXRD experiments. Analogous behaviors were noticed from **PMBC** as well, indicating that the difference in halogen atoms did not influence the phase transformations.[15,21,22] Apart from isoamyl alcohol, we observed similar phase transition and color change, when the crystals of **PMBB** and **PMBC** were exposed to other protic solvents such as methanol, ethanol, and water. Further, we observed the reversal in phase transition upon exposure to other aprotic solvent such as monoglyme, apart from acetone.

Thermal Properties. To establish the thermal stabilities as well as the phase-transition character of **PMBB** and **PMBC**, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under nitrogen gas atmosphere. TGA of **PMBB** and **PMBC** (Supporting Information, Figure S8) crystals showed no weight loss until 360 °C, thus indicating no solvent or water molecules trapped in the crystal lattice. This is in good agreement with their elemental analysis, IR, and NMR data as well (Supporting Information, Figures S5−S7).

DSC traces of **PMBB** and **PMBC** exposed to vapors of isoamyl alcohol and acetone are shown in Figure 6. For a ready comparison, DSC profiles of the as-synthesized complexes are also included. Interestingly, in all cases a single melting endotherm was observed; however, the peak values differed significantly with the nature of solvents employed. If protic solvents are used, either during synthesis or during postsynthesis vapor exposure, solids of **PMBB** and **PMBC** melted at a lower temperature (~13−15 °C) than that observed for the samples synthesized in aprotic medium (**PMBB**; mp = 174−178 °C and **PMBC**; mp = 128−131 °C). It is supported by the melting points of these compounds determined manually, vide supra. Thus, thermal properties of **PMBB** and **PMBC** are quite sensitive to the solvents employed. Solvents of recrystallization have been recognized to influence the thermal properties of the crystalline materials,[17] since the intermolecular interactions and the lattice energy of a solid are specified by medium. In these connections, the results reported herein may also serve to
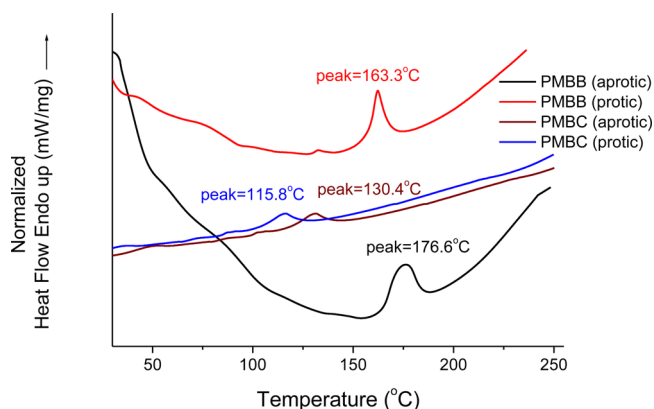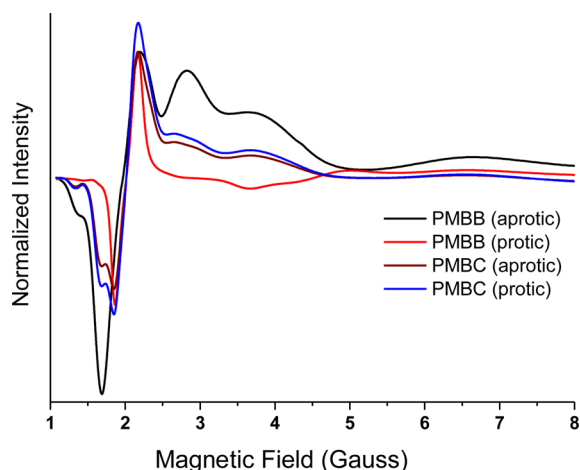
Figure 6. DSC profiles of **PMBB** and **PMBC** exposed to the isoamyl alcohol vapors (red and blue) and the as-prepared in acetone (black and wine).

indicate how environment, phase transitions, and thermal properties are linked with each other.

EPR Analyses. The paramagnetic nature of Mn(II) ion encouraged us to examine EPR activities of **PMBB** and **PMBC**. Figure 7 shows typical EPR profiles of solids of **PMBB** and


Figure 7. EPR profiles of solids of **PMBB** and **PMBC** exposed to vapors of isoamyl alcohol and acetone solvents.

PMBC exposed to vapors of isoamyl alcohol and acetone solvents. Depending on the nature of the solvent vapors the g values varied significantly: 2.0164 ± 0.0002 (for **PMBB**) and 2.0121 ± 0.0002 (for **PMBC**) exposed to isoamyl alcohol vapors, whereas 1.9446 ± 0.0003 (for **PMBB**) and 2.0011 ± 0.0006 (for **PMBC**) exposed to acetone vapors. The g values are in good agreement with the values reported for other Mn(II) complexes.[23] The observed difference in g values might be due to the difference in molecular packing of **PMBB** and **PMBC** as they are influenced by vapors of protic and aprotic solvents. Such a similar difference in g values was observed for the polymorphs of the EPR-active molecules.[24]

Switching of TL of PMBB and PMBC. We examined the suitability of **PMBB** and **PMBC** to function as reversible ON and OFF TL switches. Figure 8 shows that when crystals of **PMBB** and **PMBC** were exposed to the isoamyl alcohol vapors, their TL emission intensity sharply decreased. If these solids are then exposed to the acetone vapors, the TL emission intensity was regained. In this way, the TL light of the **PMBB** and the **PMBC** was switched back and forth, respectively, by exposing the complexes to vapors of aprotic and protic solvents for at least six cycles (Figure 8). However, the recovered light intensity was found to be less than that of the as-prepared crystals. We indeed expected such reduction in intensity, since the TL effect is maximized when good crystals are fractured.[2]

We expect that the propeller-shaped quaternary ammonium or phosphonium cations, combined with bulky counterions,[17,25] might result in frustrated ion pair contacts due to the mismatches in sizes and shapes of these ions. Nevertheless, the strong electrostatic Coulomb attraction between the counterions should prevail.[25] Therefore, such solids were demonstrated to undergo either reversible or irreversible morphological modulation depending on the surroundings.[15,21,22] It was concluded from their crystal structures that the phase transformations took place via weak intermolecular interactions, which can rearrange themselves, forming a new lattice with another set of weak interactions.[15,17,21,22] Therefore, we believe that discovered phase transformations in **PMBB** and **PMBC** may occur through changes in dihedral angles (between central phosphorus atom and aryl unit) as well as weak C–H···π and π···π intermolecular interactions between the aryl units.

The obtained experimental data as well as analysis of the TL property of **PMBB** and **PMBC** suggest that the TL emission
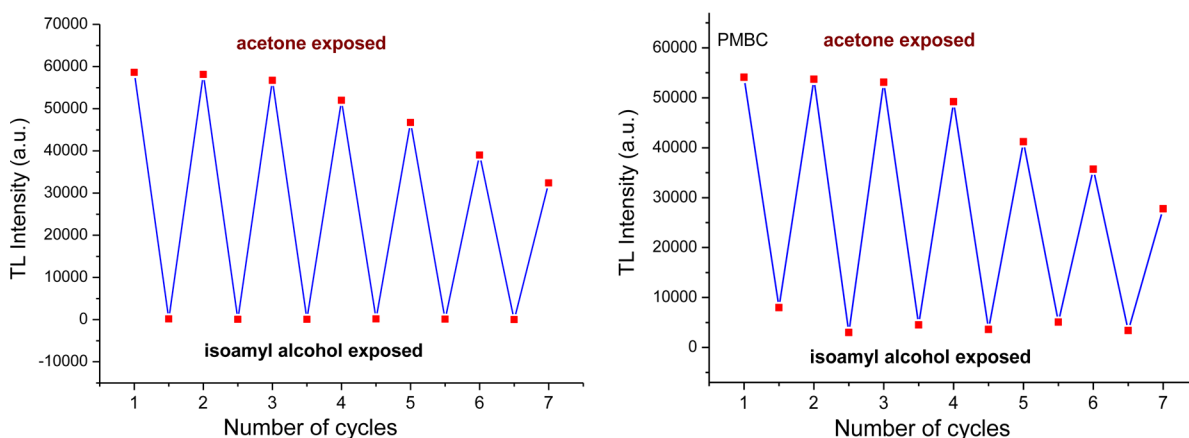
Figure 8. Modulation of TL intensity of **PMBB** (left) and **PMBC** (right) as a function of vapors exposed. The TL intensity was measured at the same experimental conditions for all samples using a Fluorolog spectrofluorometer, cf. Supporting Information, Figures S9 and S10.

seems to be affected by the crystal dynamism as well! In addition to various other factors reported to influence the TL emission,[3−5] one should consider the phase transition as well to get triboluminophors to practical functions.

CONCLUSIONS

We synthesized and investigated TL-emitting Mn(II) complexes, namely, **PMBB** and **PMBC**. Complexes synthesized in aprotic solvents such as acetone and monoglyme were found to be stable in dry air and exhibited a bright green light upon grinding. However, they underwent phase transformations while exposed to vapors of the protic solvents such as methanol, ethanol, isoamyl alcohol, and water. After the transformation, the color changed from bright green to faint green, and the TL emission dropped. Detailed analyses show that structural transformations of **PMBB** and **PMBC** were triggered by exposure to the vapors, but the vapors were not being adsorbed by the solid. Therefore, the morphology, the appearance, and the TL were recovered easily by exposing the complexes to vapors of aprotic solvents. In this manner, reversible functional characters of **PMBB** and **PMBC** can be switched by exposing these complexes to the vapors of aprotic solvents and protic solvents for at least six rounds. A merit of this research is to understand how the small structural changes, caused by environment, twist functional behaviors, in particular the TL character of certain solid materials, extremely. The complete realization will eventually lead to unique solutions to problems in other areas[1,3] such as real-time continuous monitoring of damages in civil, aerospace, military structures, and so on utilizing triboluminophors.

EXPERIMENTAL SECTION

General Information. All reactions were performed under a nitrogen gas atmosphere in oven-dried glassware. The solvents were freshly distilled prior to use. Raw materials, $MnCl_2 \cdot 4H_2O$, $MnBr_2 \cdot 4H_2O$, and methyltriphenylphosphonium bromide, were purchased from commercial source and were used as received. The PXRD patterns were recorded on a Siemens D500 diffractometer with graphite monochromated and Cu Kα radiation (λ = 1.540 56 Å). Fourier transform infrared (FT-IR) spectra were recorded using a Perkin−Elmer Rx1 instrument by using KBr pellets. EPR measurements were carried out using a Bruker EMX 10/12 X-band ESR spectrometer. DSC analyses were performed in a PerkinElmer DSC7 DSC under nitrogen gas atmosphere. The TL intensity was measured using a Fluorolog spectrofluorometer Jobin Yvon-Spex ES-3−22. Elemental analyses were carried out using Elementar Vario Micro Cube instrument. NMR spectra were recorded on 400 MHz FT-NMR spectrometer in deuterated solvents. All measurements were carried out under moisture-free conditions unless stated otherwise.

All vapor-induced phase transformation experiments were carried out at ambient temperature. The required solvent (methanol, ethanol, isoamyl alcohol, acetone, or monoglyme) was placed in the bottom compartments of the desiccators, and the **PMBB** or the **PMBC** was placed on a glass plate in the upper compartments, exposed to the solvent vapors under closed conditions.

TL measurements with a drop tower: The measurement began by placing a small pile of solids on the plexiglass plate. Solids were arranged so that it was positioned around the center of the tube. A 120 g steel ball or ceramic ball was positioned on a pull pin a distance of 90 cm above the material. The pin was pulled, and the ball fell and impacted the sample material, producing TL, which was captured by an external optical cable connected to a computer.

Preparation of PMBB. A suspension of methyltriphenylphosphonium bromide (10.0 g, 27.8 mmol) and $MnBr_2 \cdot 4H_2O$ (4.0 g, 13.9 mmol) in acetone (200−230 mL) was refluxed under N_2 for 6 h. The reaction mixture was cooled to room temperature and then filtered to remove insoluble particles. The resultant yellow colored filtrate was allowed to slowly evaporate at room temperature. After about 36−48 h, the bright green crystals so formed were isolated by filtration, washed with a small portion of cold acetone, and dried (yield 91−93%): mp 174−177 °C; IR (KBr cm^{-1}) 3864, 3432, 3159, 3055, 2963, 2888, 2810, 2594, 2217, 1984, 1919, 1822, 1582, 1428, 1326, 1187, 1101, 904, 743, 685, 495; ^{1}H NMR (400 MHz, D_2O) δ 7.6−7.9 (m, 15H), 3.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 15.6, 117.5, 129.4, 133.2 ppm; ^{31}P{^{1}H} NMR (161.9 MHz, D_2O) δ 19.8 ppm; Anal. Calcd for $C_{38}H_{36}P_2MnBr_4$: C, 49.12; H, 3.91. Found: C, 49.09; H, 3.87%.

Preparation of PMBC. This compound was synthesized following the procedure described for PMBB. However, $MnCl_2 \cdot 4H_2O$ was used instead of $MnBr_2 \cdot 4H_2O$ (yield 87−91%): mp 126−130 °C; IR (KBr cm^{-1}) 3865, 3779, 3437, 3159, 3056, 2963, 2889, 2809, 2692, 2595, 2304, 2217, 2099, 1983, 1909, 1824, 1582, 1429, 1327, 1186, 1103, 999, 904, 744, 685, 496; ^{1}H NMR (400 MHz, D_2O) δ 7.6−8.0 (m, 15H), 3.13 (s, 3H, broad) ppm; ^{13}C NMR (100 MHz, D_2O) δ 15.3, 15.8, 117.1, 117.8, 129.4, 130.2, 132.6, 134.3 ppm; ^{31}P{^{1}H} NMR (161.9 MHz, D_2O) δ 26. Four (broad) ppm; Anal. Calcd for $C_{38}H_{36}P_2MnBr_2Cl_2$: C, 54.32; H, 4.32. Found: C, 54.31; H, 4.36%.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional photographs, PXRD, IR, and NMR spectra of **PMBB** and **PMBC** compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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