Persistent room temperature blue phosphorescence from racemic crystals of 1,1-diphenylmethanol derivatives

Masaru Yamada, Kaname Ishigaki, Tatsuo Taniguchi, Takashi Karatsu

PII:	S1010-6030(20)30840-6
DOI:	https://doi.org/10.1016/j.jphotochem.2020.113043
Reference:	JPC 113043
To appear in:	Journal of Photochemistry & Photobiology, A: Chemistry
Received Date:	6 August 2020
Revised Date:	11 November 2020
Accepted Date:	11 November 2020

Please cite this article as: Yamada M, Ishigaki K, Taniguchi T, Karatsu T, Persistent room temperature blue phosphorescence from racemic crystals of 1,1-diphenylmethanol derivatives, *Journal of Photochemistry and amp; Photobiology, A: Chemistry* (2020), doi: https://doi.org/10.1016/j.jphotochem.2020.113043

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.



Persistent room temperature blue phosphorescence from racemic crystals of 1,1diphenylmethanol derivatives

Masaru Yamada^a, Kaname Ishigaki^a, Tatsuo Taniguchi^a, and Takashi Karatsu^{*a,b}

- ^a Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University,
- ^b Molecular Chirality Research Center, Chiba University,

1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan, E-mail: karatsu@faculty.chiba-u.jp.

Graphical Abstract



Highlights

- 1,1-Diphenylmethanol derivatives are one of the simplest small molecules showed persistent room temperature phosphorescence (pRTP) in their solid state.
- The λ_{max} s of pRTP are around 500 nm that is 0.75 eV smaller than those in Glassy matrices at 77K.

- 1,1-Diphenylmethanol derivatives are achiral molecules but existing as a pair of conformationally chiral racemate in the crystal.
- The interaction of racemic pair must be important factor to confine excitation energy in the crystal.

ABSTRACT

Among the six alkyldiphenylmethanol derivatives assessed in this study, five showed persistent room temperature phosphorescence (pRTP), whereas the original diphenylmethanol (**DPhHOH**) did not. pRTP is a unique luminescence phenomenon that appears only in the crystalline state and is different from the luminescence produced by dispersed molecules, such as those in a glassy solvent matrix at 77 K or a polymeric matrix. The data also suggest that pRTP appears in conjunction with a specific crystal structure. The present work demonstrates that various crystal structures show pRTP regardless of the presence or absence of weak hydrogen bonds. However, nonradiative deactivation is suppressed by both intermolecular interactions and steric regulation in the crystal, such that the emission quantum yield is dependent on the crystal structure. In addition, although the molecular structure in the crystalline state necessary for the appearance of pRTP was not fully elucidated, intermolecular interactions between face-to-face and face-toedge benzene rings appear to play a major role. Density functional theory calculations indicate that intersystem crossing is promoted in the crystalline state because the number of paths that allow this intersystem crossing is greater in a structure having weak interactions between molecules as compared to a dispersed state. **DPhHOH** did not show pRTP and is considered to have a structure based on the column-like stacking of multiple molecules. In contrast, the crystals that exhibited pRTP had pseudo racemic conformation in their crystals even though each molecule was achiral. In these racemic crystals, the interactions between pairs of molecules were important to the generation of pRTP.

Keywords: Persistent room temperature phosphorescence; 1,1-Diphenylmethanol derivatives; Crystal structure; Racemic pair; Triplet energy delocalization

1. Introduction

Recently, there have been reports concerning the solid state phosphorescence of simple organic molecules at ambient temperature and atmospheric pressure. This phenomenon is referred to as persistent room temperature phosphorescence (pRTP) or afterglow.

Because phosphorescence is originally a forbidden transition, it has a longer emission lifetime than fluorescence. Specifically, the fluorescence emission lifetime is generally 10^{-11} to 10^{-6} s [1], while the phosphorescence lifetime is 10^{-4} to 10^{1} s. In addition, phosphorescence is characterized by a lower energy emission maximum. The associated emission energy is typically lower than that observed for typical phosphorescence in a glassy solvent matrix at 77 K.

In the solid state, molecular motion is fixed and k_{nr} might become small [2], but it is important that k_p is also small in order to achieve an ultralong lifetime. However, obtaining high luminous efficiency requires that k_{nr} is less than k_p . The emission quantum yield, Φ_p , of the T₁ state can be expressed by the formula $\Phi_p = \Phi_{isc} \times k_p \times \tau_p$ where Φ_{isc} is the quantum yield of the intersystem crossing (ISC). Achieving a high Φ_p therefore requires a molecular design that raises the value of Φ_{isc} .

Phosphorescence is an extremely useful means of exciting organic Electro-Luminescence. It has been reported that organometallic complexes containing platinum group atoms emit phosphorescence with very high efficiency [2–11]. This has led to research into metal-free organic light-emitting materials for thermally activated delayed fluorescence.

In 2010, Tang and his collaborators demonstrated that benzophenone derivatives, which are not phosphorescent in solution, generate phosphorescence in the crystalline state at room temperature in air [12]. Benzophenone has a high Φ_{isc} value of 1.0, and is known to generate an excited triplet state with a high yield but also exhibits a negligible Φ_p . However, a Φ_p value of 15.9% was obtained in the crystalline state at room temperature. Tang et al. proposed that this effect was induced by the suppression of nonradiative deactivation due to intramolecular rotation and vibration following crystallization. Therefore, this phenomenon is referred to as crystallization-induced phosphorescence (CIP).

Huang and his collaborators later reported that 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-carbazole shows pRTP [13]. Single crystal X-ray structural analysis of this compound determined that Haggregates were formed in the solid and that this structure further stabilized the T₁ state by forming energy traps, thus promoting pRTP [14]. Time dependent density functional theory (TD-DFT) calculations performed for the monomer and dimer based on the crystal structure demonstrated that the number of ISC paths (that is, $S_1 \rightarrow T_n$) was increased in the dimer relative to the monomer. However, efficiency of each process is unclear. Such studies prompted additional research into pRTP.

Recently, authors reported that important insight into the impurities caused persistent room temperature phosphorescence from the crystals of carbazole derivatives [15]. This is also interesting from the crystal doping point of view. Interestingly, the first report regarding pRTP was published by Clapp in 1939, who found that the exposure of tetraphenylmethane or tetraphenylsilane crystals to light produced pRTP [16]. Much later, in 1978, Morantz et al. showed that pRTP was also obtainable from carbazole, dibenzthiophene, dibenzofuran and triphenylene crystals [17]. Following Morantz's work, there were few publications concerning the generation of pRTP by pure organic compounds, and the associated luminescence mechanism was not studied in detail. However, more recently, there have been assessments of many different organic molecules that exhibit this phenomenon.

Among the various molecules that have been found to show RTP in the solid state, several organic compounds are able to exhibit phosphorescence with a long emission lifetime of several seconds that can be visually observed [18–21]. As noted, this process is referred to as pRTP, and often generates a different wavelength from the more typical phosphorescence exhibited in glassy matrices at 77 K. Various mechanisms have been proposed for this emission, including π - π interactions that induce rigidity in crystals, association via hydrogen bonds and other phenomena that promote ISC.

Li and collaborators demonstrated that the molecular packing structure of a compound affects the appearance of pRTP. Specifically, pRTP was observed in work with a crystalline derivative [22], and then 4-(10H-phenothiazin-10-yl)benzonitrile, which produced three different crystalline polymorphs and showed that variations in the packing structure affected the pRTP characteristics [23]. Analyses of the interactions between the molecules in the three crystal structures indicated that the crystal phase forming the H-aggregate showed low luminous efficiency. The crystalline regions of these compounds evidently had the highest Φ_p values and so the molecular structure, the intermolecular interactions in the crystal and the molecular stereostructure were all related to the pRTP characteristics.

Li and co-workers established the importance of hydrogen bonding between molecules based on work with a compound without aromatic rings [24]. Kim et al. examined the pRTP behaviour of 4-bromo-2,5-bis(hexyloxy)benzaldehyde), which has aligned molecules in the crystalline state. Only weak fluorescence was obtained from this compound in solution, but the incorporation of the heavy bromine atom worked efficiently between the molecules in the crystal [25]. Since then, efforts have been made for pRTP that does not utilize the heavy atom effect [26–28].

Another useful approach to obtaining pRTP utilizes charge separation and recombination [29–32]. Yuasa and co-workers proposed that the ISC mechanism involved hyperfine coupling in radical ion pairs formed from molecules in the crystalline state [29]. In the case that a singlet radical ion pair is

generated, the ISC to the triplet excited radical ion pair occurs because the acceptor side radical and the donor side radical are situated in different magnetic field environments. Because there is a large distance between these radicals, the degree of overlap between orbitals is minimal and the transition to other levels (such as S_0) is slow. This generation of a triplet excited state is also involved in various other useful physical processes such as those occurring in organic light emitting diodes [33, 34]. The concept of fixing the molecular structure has also been applied to the development of inorganicorganic hybrid systems [35–40], bio-inspired system [41], emission color tuning [42–44], and mechanoluminescence [45].

As noted, pRTP has been actively studied in recent years and various luminescence mechanisms have been proposed. However, the reason for the long lifetimes and some parts of the luminescence mechanisms remain unclear, and there is little agreement in this area. Therefore, the design of molecules that display pRTP is still difficult, and further research is needed to predict which molecules will exhibit this phenomenon. In the present study, we determined that 1,1-diphenylmethanol derivatives (Fig. 1) show pRTP emission lifetimes of several hundred milliseconds and investigated the associated emission mechanism [46]. 1,1-Diphenylmethanol derivatives are one of the simplest small molecules showed persistent room temperature phosphorescence (pRTP) in their solid state. These pRTP are around 500 nm that is 0.75 eV smaller than those in Glassy matrices at 77K. 1,1-Diphenylmethanol derivatives are achiral molecules but existing as a pair of conformationally chiral racemate in the crystal. Interaction of the racemic pair must be important factor to confine excitation energy into multiple molecules in a crystal has been proposed by a couple of research groups in recent years [50, 51], and is considered to be an important process even in the long-lived triplet excited state proposed in this study.

<Fig. 1. The 1,1-diphenylmethanol derivatives examined in the present study.>

2. Experimental

2.1. Syntheses of **DPhEtOH**, **DPhPrOH** and **DPhcHexOH**

DPhEtOH (1,1-diphenylpropanol), DPhPrOH (1,1-diphenylbutanol), and DPhc-HexOH

(cyclohexyldiphenylmethanol) were obtained using Grignard reactions. The initial reagent was prepared from magnesium and bromobenzene in dry tetrahydrofuran (THF) and then reacted with 6.8-15.3 mmol (0.7 equivalents) of propiophenone, 1-phenylbutan-1-one or

cyclohexyl(phenyl)methanone. The products were separated using an open column (with an ethyl acetate:hexane mixture as the eluent) and purified by recrystallization. The products were obtained as white solids with yields between 62 and 72%.

DPhEtOH; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.40–7.43 (m, 4H), 7.28–7.33 (m, 4H), 7.19–7.24 (m, 2H), 2.32 (q, J=7.22 Hz, 2H), 2.07 (s, 1H), 0.88 (t, J=7.22 Hz, 3H) (Fig. S1). mp 95 °C (range of less than 1 °C). Elemental analysis (%): calculated for C₁₅H₁₆O: C, 84.87; H, 7.60; N, 0; found: C, 84.81; H, 7.62; N, 0.10.

DPhPrOH; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.39–7.42 (m, 4H), 7.28–7.32 (m, 4H), 7.19–7.23 (m, 2H), 2.24–2.27 (m, 2H), 2.08 (s, 1H), 1.25–1.33 (m, 2H), 0.93 (t, J=7.28 Hz) (Fig. S2). mp 37 °C (range of less than 1 °C). Elemental analysis (%): calculated for C₁₆H₁₈O: C, 84.91; H, 8.02; N, 0; found: C, 85.04; H, 8.05; N, 0.17

DPhc-HexOH; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.46–7.49 (m, 4H), 7.25–7.29 (m, 4H), 7.13– 7.18 (m, 2H), 2.40–2.47 (m, 1H), 2.06 (s, 1H), 0.90–1.77 (m, 10H) (Fig. S3). mp 68 °C (range of less than 1 °C). Elemental analysis (%): calculated for C₂₀H₁₈O₂N: C, 85.67; H, 8.32; N, 0; found: C, 85.61; H, 8.32; N, 0.19.

2.2. Synthesis of DPhMeOMe (1-methoxy-1,1-diphenylethane)

In a 50 ml three necked flask, 1,1-diphenylethanol (402 mg; 2.03 mmol), sodium hydride (208 mg; 2.60 mmol) and 5 ml dry THF were combined under dry nitrogen. This mixture was stirred for 30 min with cooling by ice, after which iodomethane (620 mg; 4.36 mmol) was added and the mixture was allowed to warm to room temperature and stirred for 19 h. The crude product was separated using an open column (with ethyl acetate:hexane = 1:12 as the eluent) and purified by recrystallization. The product was a white solid with a yield of 207 mg (48%).

¹H NMR (400 MHz, CDCl₃): δ ppm = 7.33 – 7.36 (m, 4H), 7.28 – 7.32 (m, 4H), 7.20 – 7.24 (m, 4H), 3.16 (s, 3H), 1.86 (s, 3H), (Fig. S4). mp 35 °C (range of less than 1 °C.) Elemental analysis (%): calculated for C₁₅H₁₆O: C, 84.87; H, 7.60; N, 0; found: C, 84.71; H, 7.60; N, 0.09.

2.3. Purification of compounds

DPhc-PrOH was purchased from the Tokyo Chemical Industry Co., Ltd. and treated with charcoal to remove pale yellowish impurities. Each compound was purified by recrystallization from hexane at room temperature (for **DPhHOH**, **DPhMeOH**, **DPhEtOH**, and **DPhc-PrOH**), from hexane at -20 °C (for **DPhPrOH** and **DPhc-HexOH**) or from methanol at -20 °C (for **DPhMeOMe**).

2.4. Instrumentation and measurement

Samples were analysed by ¹H nuclear magnetic resonance (NMR; Bruker AVANCE III-400M, 400 MHz) and also assessed by CHN elemental analysis (Perkin Elmer PE2400II). UV-vis absorption and emission spectra were acquired with JASCO V-570 and JASCO FP-8300 spectrophotometers, respectively.

Absolute emission quantum yields were determined using a JASCO FP-8300 instrument with an integrated sphere unit for solutions and a Hamamatsu photonics C11347-01 apparatus with an integrated sphere unit for solid samples. Since the wavelength intensity of the light source of the device and the wavelength sensitivity of the detector can be corrected only at wavelengths longer than 250 nm, considering the band path of the excitation light, the excitation wavelength could only be performed at 260 nm. Therefore, in the measurement of solid-state emission, the fluorescence is very close to the excitation light and it is difficult to separate this incident light. Therefore, the quantum yield of phosphorescent light appearing at a long wavelength was firstly determined by 260 nm excitation. Then the quantum yields of fluorescence were estimated by the spectral area of fluorescence and phosphorescence spectra obtained by 250 nm excitation. At this time, it was assumed that the emission spectra obtained by excitation at 260 nm are identical.

Emission lifetime measurements were performed with a HORIBA NAES-550 or IBH 5000U-CS instrument (for single photon counting) or a JASCO FP-8300 instrument. Single crystal X-ray structural analyses were carried out using a Bruker AXS SMART APEX II.

3. Results and discussion

3.1. Emission characteristics in the crystalline state

Irradiation with a UV lamp ($\lambda_{ex} = 254$ nm) produced blue emission from crystals of **DPhMeOH**, **DPhEtOH**, **DPhPrOH**, **DPhc-PrOH**, **DPhc-HexOH** and **DPhMeOMe** that remained visible for several seconds after the irradiation was stopped, indicating that pRTP was possibly generated (Fig. 2). However, in the case of the **DPhHOH**, visible light emission and pRTP could not be observed visually. <Fig. 2. Photographic images of crystals under white light and emissions under UV irradiation at $\lambda_{ex} = 254$ nm and after irradiation.>

To assess the solid-state emission characteristics of these compounds in more detail, emission spectra were acquired at room temperature (298 K). In Fig. 3, the black solid line is the emission spectrum obtained in the steady state with the excitation at $\lambda_{ex} = 250$ nm, while the red solid line is the time-resolved emission spectrum 50 ms after the excitation light was cut off. The **DPhMeOH**, **DPhEtOH**, **DPhPrOH**, **DPhc-PrOH**, **DPhc-HexOH** and **DPhMeOMe** all generated pRTP that was visible to the naked eye. This emission was characterized by time-resolved emission spectra having a similar vibrational structure around 444-508 nm. In addition, similar narrow band emission was observed at approximately 310 nm for these same compounds, and might be attributed to delayed fluorescence caused by triplet-triplet annihilation (TTA) [52], and further study must be required. In the case of the **DPhHOH**, which did not exhibit pRTP, only a broad emission spectrum having no vibrational structure was obtained, consistent with the emission spectrum in a solution state (Fig. S5).

<Fig. 3. The emission spectra of (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhPrOH**, (d) **DPhc-PrOH**, (e) **DPhc-HexOH** and (f) **DPhMeOMe**. Black solid lines: steady state emission spectra, red solid lines; time resolved spectra (delay time: 50 ms, gate width: 25 ms, $\lambda_{ex} = 250 \text{ nm}$).>

Table 1 summarizes the emission characteristics of the diphenylmethanol derivative in the solid state. It has been reported that aromatic compounds such as naphthalene have Φ_{isc} values of approximately 1- Φ_f when the energy difference between S₁ and S₀ (S₁ \rightarrow S₀) is at least 2.6 eV [29]. In the present study, this condition was satisfied, and so the values of k_p and k_{nr} + k_q [Q] presented in this table were calculated based on the Φ_{isc} = 1- Φ_f relationship. It is known that this assumption applies well to condensed polycyclic aromatic compounds, but it is uncertain whether this assumption is fit to this case because Φ_{isc} is not experimentally determined for this series of compounds. Here, bimolecular quenching processes by molecular oxygen and inevitable impurities are summarized as a rate of k_q [Q].

<**Table 1** Absorption and emission characteristics of diphenylmethanol derivatives in ethanol and in the solid state.>

The fluorescence quantum yield (Φ_f) in the solid state was determined to be higher than that in ethanol (Table 1). In general, two contrasting luminescence-related phenomena are known to occur in the solution state. One is aggregation-caused quenching (ACQ), in which aggregates are formed at a high concentration and the emission quantum yield is decreased [53]. However, nonradiative deactivation is also suppressed by aggregation, such that the emission quantum yield is increased in an effect known as aggregation-induced emission (AIE) [54]. Because Φ_f was found to be increased when the compounds were in the solid state in this study, it is considered that a phenomenon like AIE occurred. Since the structural change of the molecule is suppressed in the crystal and the transition probability from S₁ to S₀ maybe increased by good HOMO-LUMO overlap. In addition, Φ_f and Φ_{isc} may increase by the decrease of process of non-radiative deactivation.

Focusing on the solid-state phosphorescence characteristics, the Φ_p of **DPhMeOH** was very high at 14.9%, while the values for the other diphenylmethanol derivatives showing pRTP were between 3.8 and 9.1%. The τ_p values were determined to be in the range of 515-766 ms, which are extremely long luminescence lifetimes for organic compounds at room temperature (Fig. S6). The k_p calculated for the compounds for which pRTP was observed were on the order of 10^{-1} to 10^{-2} s⁻¹, while $k_{nr} + k_q[Q]$ was on the order of 10^2 s⁻¹. In prior work, an iridium complex exhibiting RTP was found to have $k_{nr} + k_q[Q]$ and k_p values as high as 10^5 s⁻¹ [55]. Therefore, the present Φ_p values were large and the τ_p values were small. In our study, low $k_{nr} + k_q[Q]$ values were obtained in conjunction with very small k_q , and pRTP with long τ_p values were observed at room temperature in ambient air.

3.2. Luminescence in ethanol

The UV-Vis absorption and emission spectra of the diphenylethanol derivatives showing pRTP in ethanol solutions (at 0.3 mM) are presented in Fig. S7. Each spectrum was found to have absorption maxima in the ranges of 211-215 nm and 258-259 nm. Based on the molar extinction coefficient for each molecule (Table 1), these absorption maxima are consistent with π - π * transitions at the benzene sites, and the less intense absorption band can be attributed to a symmetric forbidden transition [56].

A broad emission band without a vibrational structure was observed over the range of 282-286 nm for all compounds. In addition, the luminescence properties in solution were almost the same for all the derivatives, including **DPhHOH**, which did not show pRTP (Fig. S5).

3.3. Luminescence in an ethanol glassy matrix

The emission spectra of the diphenylmethanol derivatives in a glassy matrix were acquired in ethanol (at 0.3 mM) at 77 K (Fig. 4). At room temperature, only an emission maximum in the UV region was obtained, as also discussed in the preceding section, while a new blue emission was obtained in the glassy matrix. At 77 K, nonradiative deactivation was effectively suppressed by limiting the thermal motion of the molecules [13]. The emission characteristics in these glassy matrix states were almost the same for all derivatives including **DPhHOH** (Fig. S5).

<Fig. 4. The solution state emission spectra of (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhPrOH**, (d) **DPhc-PrOH**, (e) **DPhc-HexOH** and (f) **DPhMeOMe** (in ethanol, 0.3 μ M) as acquired at room temperature and 77 K ($\lambda_{ex} = 250 \text{ nm}$).>

In Fig. 5, the luminescence spectra of **DPhMeOH** in the solution state and the solid state are plotted against the energy values (in eV). Here, S_1 and T_1 are the energy levels associated with the fluorescence and phosphorescence maxima in the solution and glassy matrix and S_1^* and T_1^* are the energy levels calculated from the fluorescence and phosphorescence peaks in the time-resolved emission spectrum obtained from the solid state.

<Fig. 5. Emission spectra and energy diagrams of **DPhMeOH** in an ethanol matrix at 77 K and in the crystalline state at ambient temperature.>

In the solid state, light emission occurs based on transitions from the S_1^* and T_1^* states. The energy difference between S_1 and S_1^* , ΔE ($S_1S_1^*$), is 0.40 eV while that between T_1 and T_1^* , ΔE ($T_1T_1^*$), is 0.75 eV. These values indicate that the triplet state was more stabilized than the singlet state. This trend was found to be common to all the compounds that showed pRTP in this study, and all showed equivalent emission behaviour. These findings suggest that the excited state was stabilized by the common structure involved in the examined molecules. That is, phosphorescence generated from the stable T_1^* state was observed as pRTP. Further detailed investigation is required to understand energy aspect of pRTP. In addition, nonradiative transition obeys to energy gap low. In this sense, stabilization of T_1^* state may affect on knr. However, these compounds may have less susceptible small k_{nr} .

The time-resolved emission spectra acquired from these compounds in the solid state were similar, although the steady-state emission behaviour was different for each compound. In the case of each of **DPhEtOH**, **DPhc-PrOH** and **DPhc-HexOH**, strong fluorescence resulting from S₁ (like the state in solution) was observed, whereas **DPhMeOH** also exhibited significant fluorescence but from the S₁* state (stabilized state). The **DPhPrOH** and **DPhMeOMe** showed both type of intense fluorescence from S₁ and the S₁* state. Therefore, in the solid state, light emission from single molecules was observed just as in the solution state, and so photophysical processes from the S₁, S₁*, T₁ and T₁* states occurred. There were differences between the compounds, and no emission from T₁ was observed in the case of phosphorescence, indicating that emission from T₁* occurred preferentially. The melting points of **DPhPrOH** and **DPhMeOMe**, for which fluorescence from S₁ and S₁* was observed, were 37 and 35 °C, respectively, and so were lower than those of

the other diphenylmethanol derivatives (**DPhHOH**: 67 °C, **DPhMeOH**: 81 °C, **DPhEtOH**: 95 °C, **DPhc-PrOH**: 86 °C, **DPhc-HexOH**: 68 °C)

This suggests that weak intermolecular interactions in the solid state were related to the appearance of fluorescence.

3.4. Luminescent properties in PMMA thin films

Kim et al. reported that pRTP was observed upon dispersing a phosphorescent material in a poly(methyl methacrylate) (PMMA) matrix, which provided a rigid environment that suppressed radiationless deactivation [57]. We also employed a PMMA matrix in conjunction with the diphenylmethanol derivatives (Fig. S8). Each of these compounds generated a fluorescence spectrum having an emission maximum similar to that seen in the solution state, and no phosphorescence was observed in spite of the use of a more rigid environment than in the ethanol solutions. In the case of fluorene derivative, energy transfer from the compound to the PMMA was observed [58]. However, in this case no further detailed experiment was performed. This finding suggests that a rigid environment alone was insufficient to promote pRTP, and that the specific structure in the crystalline state may be a major factor related to inducing this type of emission.

3.5. Single crystal X-ray structural analysis

In order to obtain detailed information regarding the molecular packing structures, we attempted to prepare single crystals of each compound by a solvent evaporation method [59]. Single crystals of **DPhMeOH**, **DPhEtOH**, **DPhc-PrOH** and **DPhc-HexOH** were obtained by allowing saturated hexane solutions of each compound to stand in the dark at room temperature. Single crystals of **DPhHOH** were obtained in the same manner from a saturated nitromethane solution. The resulting crystallographic data are summarized in Fig. 6 and Table S1 [60].

<**Fig. 6.** Single crystal structure packing diagrams for (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH**, (d) **DPhc-HexOH** and (e) **DPhHOH**. Yellow or orange molecules in (a), (d) and (e) are in the adjacent crystal lattice.>

All the compounds that showed pRTP had similar structures (two benzene rings and a hydroxy group), and the luminescent behaviour of the crystals showed a similar pRTP emission that was clearly different from that obtained in the PMMA thin film state or solution state. These data suggest that pRTP resulted from a common interaction in the crystal structures of these compounds. The structures of those achiral molecules in the crystals are taking pseudo racemic conformations, which is a pair of mirror images (Fig. S9).

The effect of intermolecular interactions can be discussed by assessing the single crystal structures of **DPhMeOH**, **DPhEtOH**, **DPhc-PrOH**, **DPhc-HexOH** and **DPhHOH**, all of which gave single crystals. It can

be assumed that hydrogen bonds or $\pi - \pi$ interactions were present between pairs of molecules in these crystals regardless of the unit cell or Z value, with the exception of **DPhHOH**, which showed a columnar stacking structure. The intermolecular interactions in the crystal structures (excluding the face-to-face π - π interactions) and the associated distances (in Å) are shown in Fig. 7. Here, values in red indicate that the distances between atoms are shorter than the sum of the van der Waals radii, while values in parentheses for the edge-to-face interactions represent the angles between the plane of the benzene ring and the line connecting the hydrogen with the centre of the ring (Fig. S10a). In previous studies, compounds that expressed pRTP were found to form hydrogen bonds in the crystal [13]. However, even though all the present compounds except DPhMeOMe had a hydroxy group, only DPhMeOH, and DPhHOH incorporated a hydroxy group positioned so as to form a hydrogen bond. Since the distance between the oxygen atoms in the two hydroxy groups on adjacent molecules was greater than 0.27 Å, which equates to a typical hydrogen bonding distance [61], it appears that weak hydrogen bonds were present. In addition, **DPhMeOMe** (in which the hydroxy group is replaced by a methoxy group) also showed pRTP, meaning that hydrogen bonding was not essential for pRTP to be generated by the compounds of this study. Although there was no strong interaction common to all these molecules, such as hydrogen bonding, there were various weak interactions in each crystal structure, as a result of intermolecular forces and steric restrictions, that suppressed nonradiative deactivation in the crystalline state.

<**Fig. 7**. Coupled A, B, C, and D intermolecular interactions in the crystals of (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH**, (d) **DPhc-HexOH** and (e) **DPhHOH**. Colors in parentheses correspond to the molecular color in the packing diagram in Fig. 6.>

We next considered π - π interactions, which were the only common interactions among these diphenylmethanol derivatives. These π - π interactions were based on a stacking structure resulting from edge-to-face interactions in the case that the benzene rings were arranged in a T shape or face-to-face interactions where the benzene rings were arranged in parallel [62]. Because there have been many reports that pRTP is caused by face-to-face π - π (CH/ π) interactions [14, 22], the crystal substructures having the strongest face-to-face π - π interaction forces are presented in Figs. 8 and 9. Here, θ is the angle between the planes of the two benzene rings and d is the distance between the centres of gravity of the two benzene rings (in Å). With regard to the values in parentheses, the first is the shortest distance between the carbon atoms of the two facing benzene rings while the second is the distance between the centre of gravity of the benzene ring and the intersection of perpendicular lines drawn on the planes of the benzene rings facing each other (Fig. S10b). If both values are small, this indicates a larger degree of overlap of the two benzene rings and thus a stronger interaction.

<**Fig. 8.** Coupled C, B, A and B intermolecular interactions in crystalline (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH** and (d) **DPhc-HexOH**, respectively.>

<**Fig. 9.** Coupled B (lower), C (upper left) and D (upper right) intermolecular interactions in **DPhHOH**.>

It has been established that phenylboronic acid derivatives exhibiting pRTP show long-range face-to-face $\pi - \pi$ interactions even when the distance between the centres of gravity of the two benzene rings is in the range of 5.0-6.0 Å [63]. In the present work, the distance between the centres of gravity was in the same range, and the two benzene rings were arranged almost in parallel. Assuming that the strength of the face-to-face $\pi - \pi$ interactions depends on the distance between the centres of gravity, the strength should decrease in the order of **DPhHOH** > **DPhMeOH** > **DPhEtOH** > **DPhc-PrOH** > **DPhc-HexOH**. Although there have been reports that the Φ_p and τ_p values associated with pRTP are proportional to the strength of the face-to-face $\pi - \pi$ interactions [22], no correlation was found in this work. In addition, although the **DPhHOH** did not show pRTP, it had the strongest interactions. Therefore, we assessed another common phenomenon: edge-to-face $\pi - \pi$ interactions. Assuming that the strength of these interactions was dependent on the distance between the nearest hydrogen atom and the benzene ring, the order should decrease in the order of **DPhc**-PrOH > DPhEtOH > DPhHOH > DPhc-HexOH > DPhMeOH. However, there was no evident correlation between the luminescent properties and this order. The Φ_p and τ_p are determined by k_{nr} , which in turn is suppressed by the restricted molecular motion that results from intermolecular interactions. However, it is interesting to note that the pRTP emission appeared at almost the same wavelength for each compound, although the interactions between molecules were not consistent despite the similar structures of these molecules.

The present crystals composed of achiral molecules had a fixed conformation and their space groups were either chiral (**DPhMeOH**) or racemic (with the exception of **DPhMeOH**). Examining pairs of molecules that may interact from a fixed conformation established that either racemic or chiral pairs were obtained (Fig. 7). Racemic pairs such as those produced by **DPhMeOH** (Coupled A, B and C), **DPhEtOH** (Coupled A and B) and **DPhc-PrOH** (Coupled A and B) made greater contributions to the stabilization of the crystal compared to pairs having the same chirality, based on both CH/ π and π - π interactions. These pairs are believed to have functioned as cages that trapped and confined the excitation energy. Compact packing of racemic crystals is known as the Wallach's rule [64–66].

The crystal structure of **DPhHOH**, which had a similar structure to those of the other diphenylmethanol derivatives but did not generate pRTP, indicates the presence of π - π interactions and strong intermolecular forces. In addition, a continuous column of Coupled C and Coupled D molecules can be seen along the c-axis in Fig. 10 (The molecules in each column, shown in blue and green, have the same chirality and adjacent

columns are composed of different enantiomers). This packing structure resulted in the strongest face-to-face $\pi-\pi$ interactions among the diphenylmethanol derivatives assessed in this work. In addition, there was a continuous packing structure both between pairs of molecules and between greater numbers of molecules stacked on top of each other. It is therefore probable that pRTP was not observed from this compound due to ACQ [28, 67]. This column like structure composed of strong packing by the same enantiomer may cause delocalization of triplet excitation energy or migration of triplet excitation energy was confined in racemic pairs of such as **DPhMeOH** as similar to the concept of multimer proposed to the singlet excited state [50, 51]. Based on the above discussion, $\pi-\pi$ interactions are evidently an important factor in the appearance of pRTP, but further investigation is needed to clearly determine the structural characteristics that cause pRTP. We already started experiment along this direction. In particular, the possibility of preventing ACQ should be examined.

<Fig. 10. Aggregate formation by hydrogen bonding in DPhHOH.>

3.6. DFT calculations

Using the crystal structures obtained by single crystal X-ray structural analyses, TD-DFT calculations were performed for both the ground and excited states of single molecules and pairs of molecules [68]. The M062X functional and 6-31G (d) basis function were used [14]. The calculation results are summarized in Fig. 11, Fig. S11-S15 (MO contour of the coupled molecules) and Table S2-S16. It is generally believed that two factors are necessary for efficient $S_1 \rightarrow T_n$ ISC. The first is that the energy gap between S1 and T_n must be within 0.3 eV, the second is that S_1 and T_n must have the same symmetry components capable of enabling ISC [14,23].

<**Fig. 11.** T_n states related to ISC in (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH** and (d) **DPhc-HexOH**.>

The T_n shown in red in Fig. 11 are those that promote ISC based on the DFT calculations. The data for the four compounds that showed pRTP indicate that the number of T_n capable of enabling ISC was greater for pairs of molecules than for single molecules. As such, a crystal structure existed for each that promoted ISC to a greater extent than in a dispersed state (such as in solution) even efficiency of each process was unclear. In future, calculation by using spin orbit coupling matrix element (SOCME) between S₁ and T_n [69]. Further discussion about ISC in the crystalline state will be done after accumulating more data in future.

4. Conclusions

In this study, we found that pRTP was exhibited by **DPhMeOH**, **DPhEtOH**, **DPhc-PrOH**, **DPhc-HexOH**, **DPhPrOH** and **DPhMeOMe** in their crystal states. This is a specific type of luminescence that is observed only in the crystal state and is different from the luminescence generated in a state in which the molecules are dispersed, such as in a solution, glassy matrix or PMMA. It has been suggested that this is caused by a unique structure formed in the crystal.

These crystal structures generated pRTP regardless of the presence or absence of weak hydrogen bonds, and nonradiative deactivation of the molecules was suppressed by intermolecular interactions and steric regulation in the crystals. As such, the emission quantum yield was improved. Those crystalline materials that expressed pRTP had racemic space groups, and the interaction between racemic pairs played a major role. Computational may propose that ISC was promoted in the crystalline state because the number of transition states promoting ISC was greater than in the dispersed state even efficiency of each process was unclear. Therefore, this is considered to be one of the factors that caused pRTP to appear.

The molecules studied in the crystalline state were found to possess newly stabilized S_1^* and T_1^* states, and emissions from S_1 , S_1^* and T_1^* states were found at ambient temperature. It is likely that observed decreases in emission energy were caused by interactions between racemic pairs of molecules.

Authorship statement

All authors contributed in the following manner:

Conception and design of study, analysis and/or interpretation of data. Revising the manuscript critically for important intellectual content.

M. Y. contributed in the acquisition of data and analysis, T. I. contributed in the acquisition and analysis of X-ray single crystallography.

Declaration of Competing Interest

We declare no conflict of interest.

Acknowledgments

This work was supported by a KAKENHI Grant-in-Aid for Scientific Research (no. 26288111) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and also received funding from the Strategic Priority Research Promotion Program (Chiral Materials Science) at Chiba University. This work was also performed under the Five-star Alliance Research Program within NJRC Materials & Devices. The authors thank Professors Masami Sakamoto and Hyuma Masu and Dr. Naohiro Uemura for providing support during the single crystal X-ray structural analyses. The authors also acknowledge the Center for Analytical

<u>Journal Pre-proof</u>

Instrumentation for performing absolute emission quantum yield measurements, single photon counting, ¹H NMR spectroscopy and MS analyses.

Appendix A. Supplementary data Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020.

Journal Pre-proof

References

- N. J. Turro, V. Ramamurthy, J. C. Scaiano, "Modern molecular photochemistry of organic molecules" University Science Books, 2010.
- [2] K. Horie, I. Mita, Photochemistry in polymer solid. Decay of benzophenone phosphorescence in poly(methyl methacrylate), Chem. Phys. Lett., 93 (1) (1982) 61–65.
- [3] R. C. Evans, P. Douglas, C. J. Winscom, Coordination complexes exhibiting room-temperature phosphorescence: Evaluation of their suitability as triplet emitters in organic light emitting diodes, Coord. Chem. Rev. 250 (2016) 2093–2126.
- [4] H. Yersin, Ed. "Highly efficient OLEDs with phosphorescent materials" Wiley VCH: Berlin, Germany (2007).
- [5] D. Tanaka, H. Sasabe, Y.-J. Li, S.-J. Su, T. Takeda, J. Kido, Ultra high efficiency green organic lightemitting devices, Jpn. J. Appl. Phys. 46 (2007) L10–12.
- [6] C. W. Tang, S. A. Vanslyke, Organic electroluminescent diodes, Appl. Phys. Lett. 51 (12) (1987) 913– 915.
- [7] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, Highly efficient phosphorescent emission from organic electroluminescent devices, Nature, 395 (1998) 151– 154.
- [8] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, Very high-efficiency green organic light-emitting devices based on electrophosphorescence, Appl. Phys. Lett. 75 (1) (1999) 4–6.
- [9] L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong, J. Kido, Recent progresses on materials for electrophosphorescent organic light- emitting devices, Adv. Mater. 23 (8) (2011) 926–952.
- [10] C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, Endothermic energy transfer: A mechanism for generating very efficient high-energy phosphorescent emission in organic materials, Appl. Phys. Lett. 79 (13) (2001) 2082–2084.
- [11] R. J. Holmes, D. W. D'Andrade, S. R. Forrest, X. Ren, J. Li, M. E. Thompson, Efficient, deep-blue organic electrophosphorescence by guest charge trapping, Appl. Phys. Lett. 83 (18) (2003) 3818.
- [12] T. Karatsu, M. Takahashi, S. Yagai, A. Kitamura, Photophysical properties of substituted homoleptic and heteroleptic phenylimidazolinato Ir(III) complexes as a blue phosphorescent material, Inorg. Chem. 52 (21) (2013) 12338–12350.
- [13] W. Z. Yuan, X. Y. Shen, H. Zhao, J. W. Y. Lam, L. Tan, P. Lu, C. Wang, Y. Liu, Z. Wang, Q. Zheng, J. Z. Sun, Y. Ma, B. Z. Tang, Crystallization-induced phosphorescence of pure organic luminogens at room temperature, J. Phys. Chem. C. 114 (13) (2010) 6090–6099.
- [14] Z. An, C. Zheng, Y. Tao, R. Chen, H. Shi, T. Chen, Z. Wang, H. Li, R. Deng, X. Liu, W. Huang, Stabilizing triplet excited states for ultralong organic phosphorescence, Nature Mater. 14 (2015) 685–690.

- [15] C. Chen, Z. Chi, K. C. Chong, A. S. Batsanov, Z. Yang, Z. Mao, Z. Yang, B. Liu, Carbazole isomers induce ultralong organic phosphorescence. Nature Mater. DOI: 10.1038/s41563-020-0797-2.
- [16] D. B. Clapp, The phosphorescence of tetraphenylmethane and certain Substances, J. Am. Chem. Soc. 61 (2) (1939) 523–524.
- [17] C. S. Bilen, N. Harrison, D. J. Morantz, Unusual room temperature afterglow in some crystalline organic compounds, Nature, 271 (1978) 235–237.
- [18] S. Hirata, Recent advances in materials with room- temperature phosphorescence: Photophysics for triplet exciton stabilization, Adv. Optical Mater., 5 (17) (2017) 1700116 (1–50).
- [19] W. Zhao, Z. He, J. W. Y. Lam, Q. Peng, H. Ma, Z. Shuai, G. Bai, J. Hao, B. Z. Tang, Rational molecular design for achieving persistent and efficient pure organic room temperature phosphorescence, Chem, 1 (2016) 592–602.
- [20] S. Xu, R. Chen, C. Zheng, W. Huang, Excited state modulation for organic afterglow: Materials and applications, Adv. Mater. 28 (45) (2016) 9920–9940.
- [21] N. Nishimura, Z. Lin, K. Jinnai, R. Kabe, C. Adachi, Organic long- persistent luminescence: Many exciplex systems exhibit organic long- persistent luminescence, Adv. Functional Mater. 22 (2020) 2070138.
- [22] J. Yang, X. Zhen, B. Wang, X. Gao, Z. Ren, J. Wang, Y. Xie, J. Li, Q. Peng, K. Pu, Z. Li, The influence of the molecular packing on the room temperature phosphorescence of purely organic luminogens, Nature Commun. 9 (2018) 840.
- [23] J. Yang, Z. Ren, B. Chen, M. Fang, Z. Zhao, B. Z. Tang, Q. Peng, Z. Li, Three polymorphs of one luminogen: how the molecular packing affects the RTP and AIE properties? J. Mater. Chem. C, 5 (2017) 9242–9246.
- [24] M. Fang, J. Yang, X. Xiang, Y. Xie, Y. Dong, Q. Peng, Q. Li, Z. Li, Unexpected roomtemperature phosphorescence from a non-aromatic, low molecular weight, pure organic molecule through the intermolecular hydrogen bond, Mater. Chem. Front. 2 (2018) 2124–2129.
- [25] O. Bolton, K. Lee, H. J. Kim, K. Y. Lin, J. Kim, Activating efficient phosphorescence from purely organic materials by crystal design, Nature Chem. 3 (3) (2011) 205–210.
- [26] I. Bhattacharjee, S. Hirata, Highly efficient persistent room-temperature phosphorescence from heavy atom-free molecules triggered by hidden long phosphorescent antenna, Adv. Mater. (Weinheim, Germany) (2020), ahead of print. DOI:10.1002/adma.202001348.
- [27] S. Hirata, Roles of localized electronic structures caused by π degeneracy due to highly symmetric heavy atom-free conjugated molecular crystals leading to efficient persistent room-temperature phosphorescence, Adv. Science (Weinheim, Germany), 6(14) (2019), DOI:10.1002/advs.201900410.
- [28] S. Hirata, Intrinsic analysis of radiative and room-temperature nonradiative processes based on triplet state intramolecular vibrations of heavy atom-free conjugated molecules toward efficient persistent room-temperature phosphorescence, J. Phys. Chem. Lett. 9 (15) (2018) 4251-4259.

- [29] S. Kuno, H. Akeno, H. Ohtani, H. Yuasa, Visible room-temperature phosphorescence of pure organic crystals via a radical-ion-pair mechanism, Phys.Chem.Chem.Phys. 17 (2015) 15989– 15995.
- [30] L. Huang, J. Liu, L Liu, Q. Yang, Z. Ma, X. Jia, D-A-D' type organic molecule with persistent phosphorescence exhibiting dual-mode mechanochromism, Dyes Pigm. 173 (2020) 107963.
- [31] H. Han, E.-G. Kim, Dielectric effects on charge-transfer and local excited states in organic persistent room-temperature phosphorescence, Chem. Mater. 31(17) (2019) 6925–6935.
- [32] W. Huang, B. Chen, G. Zhang, Persistent room-temperature radicals from anionic naphthalimides: Spin pairing and supramolecular chemistry, Chem. Eur. J. 25(54) (2019) 12497–12501.
- [33] Z. Lin, R. Kabe, K. Wang, C. Adachi, Influence of energy gap between charge-transfer and locally excited states on organic long persistence luminescence, Nature Commun. 11, (2020) s41467– 019–14035–y.
- [34] R. Kabe, C. Adachi, Organic long persistent luminescence, Nature, 550 (2017) 384–387.
- [35] X. Yang, D. Yan, Long- lived phosphorescence: Strongly enhanced long- lived persistent room temperature phosphorescence based on the formation of metal–organic hybrids, Adv. Optical Mater. 4 (2016) 897–905.
- [36] H. Mieno, R. Kabe, N. Notsuka, M. D. Allendorf, C. Adachi, Long- lived room- temperature phosphorescence of coronene in zeolitic imidazolate framework ZIF- 8, Adv. Optical Mater. 4 (2016) 1015–1021.
- [37] X.-G. Yang, X.-M. Lu, Z.-M. Zhai, J.-H. Qin, X.-H. Chang, M.-L. Han, F.-F. Li, L.-F. Ma, π-Type halogen bonding enhanced the long-lasting room temperature phosphorescence of Zn(II) coordination polymers for photoelectron response applications, Inorg. Chem. Frontiers, 7(11) (2020) 2224–2230.
- [38] Y. Li, T. Gai, Y. Lin, W. Zhang, Eight Cd(II) coordination polymers with persistent room-temperature phosphorescence: intriguing dual emission and time-resolved afterglow modulation, Inorg. Chem. Frontiers, 7(3) (2020) 777–785.
- [39] X. Chen, Z.-F. Liu, W. Jin, The effect of electron donation and intermolecular interactions on ultralong phosphorescence lifetime of 4-carnoyl phenylboronic acids, J. Phys. Chem. A, 124(14) (2020) 2746– 2754.
- [40] S. Yang, D. Wu, W. Gong, Q. Huang, H. Zhen, Q. Ling, Z. Lin, Highly efficient room-temperature phosphorescence and afterglow luminescence from common organic fluorophores in 2D hybrid perovskites, Chem. Science, 9(48) (2018) 8975–8981.
- [41] Y. Wang, S. Tang, Y. Wen, S. Zheng, B. Yang, W. Z. Yuan, DNA inspirited rational construction of nonconventional luminophores with efficient and color-tunable afterglow, ChemRxiv (2020), 1–16.
- [42] J.-X. Wang, Y.-G. Fang, C.-X. Li, L.-Y. Niu, W.-H. Fang, G. Cui, Q.-Z. Yang, Time-dependent afterglow color in a single-component organic molecular crystal, Angew. Chem., Inter. Ed. 59(25) (2020) 10032–10036.
- [43] Y. Mu, B. Xu, Z. Yang, H. Wen, Z. Yang, S. K. B. Mane, J. Zhao, Y. Zhang, Z. Chi, B. Z. Tang, Reversible and continuous color-tunable persistent luminescence of metal-free organic materials by

"self"-interface energy transfer, ACS Appl. Mater. Interfaces, 12(4) (2020) 5073–5080.

- [44] S. K. B. Mane, Y. Mu, E. Ubba, Z. Yang, J. Zhao, Z. Chi, Tuning the organic persistent roomtemperature phosphorescence through aggregated states, J. Mater. Chem. C, 7(48) (2019) 15219– 15224.
- [45] Y. Xie, Z. Li, The development of mechanoluminescence from organic compounds: breakthrough and deep insight, Mater. Chem. Frontiers, 4(2) (2020) 317-331.
- [46] L. Favereau, C. Quinton, C. Poriel, T. Roisnel, D. Jacquemin, J. Crassous, Persistent organic roomtemperature phosphorescence in cyclohexane-trans-1,2-bisphthalimide derivatives: The dramatic impact of heterochiral vs homochiral interactions, J. Phys. Chem. Lett. (2020), ahead of print. DOI:10.1021/acs.jpclett.0c01816.
- [47] Y. Wang, J. Yang, Y. Tian, M. Fang, Q. Liao, L. Wang, W. Hu, B. Z. Tang, Z. Li, Persistent organic room temperature phosphorescence: what is the role of molecular dimers? Chemical Science, 11(3) (2020) 833-838.
- [48] K. Narushima, Y. Kiyota, T. Mori, S. Hirata, M. Vacha, Suppressed triplet exciton diffusion due to small orbital overlap as a key design factor for ultralong-lived room-temperature phosphorescence in molecular crystals, Adv. Mater. (Weinheim, Germany), 31(10) (2019), DOI:10.1002/adma.201807268.
- [49] The abbreviations of compounds are expressed as derivatives of diphenylmethanol so that the differences in the alkyl groups are noticeable.
- [50] T. Hinoue, Y. Shigenoi, M. Sugino, Y. Mizobe, I. Hisaki, M. Miyata, N. Tohnai, Regulation of pstacked anthracene arrangement for fluorescence modulation of organic solid from monomer to excited oligomer emission, Chem. Eur. J. 18 (15) (2012), 4634–4643.
- [51] A. Sakai, E. Ohta, Y. Yoshimoto, M. Tanaka, Y. Matsui, K. Mizuno, H. Ikeda, New fluorescence domain "Excited Multimer" formed upon photoexcitation of continuously stacked diaroylmethanatoboron difluoride molecules with fused π- orbitals in crystals, Chem. Eur. J. 21 (50) (2015), 18128–18137.
- [52] S. Makishima, K. Yoshihara, A. Inoue, K. Tokumaru, M. Sano, M. Toyama, Y. Nishijima, S. Ichimura, M. Zama, M. Takakusa, "Keiko genshou (Fluorescent Phenomenon)" Kyoritsu Shuppan Co. Ltd., Tokyo, 1975.
- [53] R. Hu, N. L. C. Leung, B. Z. Tang, AIE macromolecules: syntheses, structures and functionalities, Chem. Soc. Rev. 43 (2014) 4494–4562.
- [54] Z. Yang, W. Qin, N. L. C. Leung, M. Arseneault, J. W. Y. Lam, G. Liang, H. H. Y. Sung, I. D. Williams, B. Z. Tang, A mechanistic study of AIE processes of TPE luminogens: Intramolecular rotation vs. configurational isomerization, J. Mater. Chem. C, 4 (2016) 99–107.
- [55] A. Endo, K. Suzuki, T. Yoshida, S. Tobita, M. Yahiro, C. Adachi, Measurement of photoluminescence efficiency of Ir(III) phenylpyridine derivatives in solution and solid-state films, Chem. Phys. Lett. 460 (2008) 155–157.
- [56] M. Hesse, H. Meier, B. Zeeh, "Spectroscopic methods in organic chemistry" 2nd ed., G. Thieme Verlag KG. Stuttgart, Germany.

- [57] D. Lee, O. Bolton, B. C. Kim, J. H. Youk, S. Takayama, J. Kim, Room temperature phosphorescence of metal-free organic materials in amorphous polymer matrices, J. Am. Chem. Soc. 135 (16) (2013) 6325–6329.
- [58] S. Hirata, K. Totani, J. Zhang, T. Yamashita, H. Kaji, S. R. Marder, T. Watanabe, C. Adachi, Efficient persistent room temperature phosphorescence in organic amorphous materials under ambient conditions, Adv. Funct. Mater., 23 (27) (2013) 3386–3397.
- [59] R. Hirayama, "Organic compound crystal production handbook–Principles and know–how–" Maruzen Publishing Co., Ltd., Tokyo, 2008.
- [60] Crystal structures of DPhHOH (CCDC numbers 931400, 684396, 108059, 1306598), DPhMeOH (CCDC1125889), DPhEtOH (CCDC1136437) have been reported, however, no report for DPhPrOH, DPhc-PrOH, and DPhc-HexOH.
- [61] G. R. Desiraju, T. Steiner, "The weak hydrogen bond: In stractural chemistry and biology", Oxford Press, New York, 1999.
- [62] M. Nishio, "New edition, introduction of intermolecular forces for organic chemistry" Kodansha Scientific, Tokyo, 2008. This content is partly in M. Nishio, M. Hirota, Y. Umezawa "The CH/π Interaction: Evidence, Nature, and Consequences" Wiley-VHC, 1998.
- [63] Z. Chai, C. Wang, J. Wang, F. Liu, Y. Xie, Y.-Z. Zhang, J.-R. Li, Q. Lia, Z. Li, Abnormal room temperature phosphorescence of purely organic boron-containing compounds: the relationship between the emissive behavior and the molecular packing, and the potential related applications, Chem. Sci. 8 (2017) 8336–8344.
- [64] O. Wallach, Zur kenntniss der terpene und der ätherischen oele, Liebigs Ann. Chem., 286 (1895) 90–118.
- [65] O. Wallach, Zur kenntniss der terpene und der ätherischen oele. Ueber gebromte derivate der carvonreihe, Liebigs Ann. Chem., 286 (1895) 119–143.
- [66] C. P. Brock, W. B. Schweizer, J. D. Dunitd, On the validity of Wallach's rule: On the density and stability of racemic crystals compared with their chiral counterparts, J. Am. Chem. Soc. 113 (26) (1991) 9811–9820.
- [67] K. Narushima, Y. Kiyota, T. Mori, S. Hirata, M. Vacha, Suppressed triplet exciton diffusion due to small orbital overlap as a key design factor for ultralong-lived room-temperature phosphorescence in molecular crystals, Adv. Mater., 31 (10) (2019) 1807268.
- [68] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K.

Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT, 2018.

[69] B. Song, W. Shao, J. Jung, S.-J. Yoon, J. Kim, Organic Light-Emitting Diode Employing Metal-Free Organic Phosphor, Appl. Mater. Interfaces, 12 (5) (2020) 6137–6143.

Journal

Table 1

Absorption and emission characteristics of diphenylmethanol derivatives in ethanol and in the solid state^a).

	In ethanol					Solid state						
	Absorption λ_{max} / nm		$\lambda_{\rm f}$	$\Phi_{\rm f}$	$\lambda_p(77K)$	$\lambda_{\rm f}$	$\Phi_{\rm f}$	λ_p	$\Phi_{\rm p}$	τ_{T}	\mathbf{k}_{p}	$k_{nr}\!\!+\!\!k_q[Q]$
	$(\epsilon \ / \ M^{\text{-l}} cm^{\text{-l}})$		/ nm	/ %	/ nm	/ nm	/ %	/ nm	/ %	/ ms	/ s ⁻¹	/ s ⁻¹
DPhMeOH	213 (8990),	258 (360)	282	3.1	350, 370, 384	310	90.4	444, 475, 503	8.3	552	1.6	0.24
DPhEtOH	214 (9230),	259 (400)	283	3.3	349, 371, 383	285	61.1	448, 478, 504	6.0	515	0.30	1.6
DPhPrOH	213 (9100),	259 (383)	283	3.0	349, 370, 383	284, 309	46.4	448, 479, 507	3.8	589	0.12	1.6
DPhc-PrOH	213 (8850),	258 (350)	282	6.0	350, 370, 384	291	62.2	450, 478, 504	8.6	648	0.35	1.2
DPhc-HexOH	211 (9160),	259 (373)	286	2.5	349, 384	285	75.5	449, 480, 508	7.6	654	0.47	1.1
DPhMeOMe	215 (9280),	258 (453)	282	4.4	351, 372, 385	285, 308	67.7	449, 480, 508	9.1	766	0.37	0.94
DPhHOH	213 (9230),	259 (417)	282	3.9	349, 369, 384	283	55.4	N.D.	N.D.	N.D.	-	-

a) For data analysis, relation of $\Phi_{isc} = 1 - \Phi_f$ is assumed, and also following equations were used, $k_p = \Phi_p / (\Phi_{isc} \times \tau_T)$ and $k_{nr} + k_q[Q] = (1 / \tau_T) - k_p$.



Fig. 1. The 1,1-diphenylmethanol derivatives examined in the present



Fig. 2. Photographic images of crystals under white light and emissions under UV irradiation at $\lambda_{ex} = 254$ nm and after irradiation.



Fig. 3. The emission spectra of (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhPrOH**, (d) **DPhc-PrOH**, (e) **DPhc-HexOH** and (f) **DPhMeOMe**. Black solid lines: steady state emission spectra, red solid lines; time resolved spectra (delay time: 50 ms, gate width: 25 ms, $\lambda_{ex} = 250$ nm).



Fig. 4. The solution state emission spectra of (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhPrOH**, (d) **DPhc-PrOH**, (e) **DPhc-HexOH** and (f) **DPhMeOMe** (in ethanol, 0.3 μ M) as acquired at room temperature and 77 K ($\lambda_{ex} = 250$ nm).



Fig. 5. Emission spectra and energy diagrams of **DPhMeOH** in an ethanol matrix at 77 K and in the crystalline state at ambient temperature.



Fig. 6. Single crystal structure packing diagrams for (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH**, (d) **DPhc-HexOH** and (e) **DPhHOH**. Yellow or orange molecules in (a), (d) and (e) are in the adjacent crystal lattice.



Fig. 7. Coupled A, B, C, and D intermolecular interactions in the crystals of (a) DPhMeOH, (b) DPhEtOH,
(c) DPhc-PrOH, (d) DPhc-HexOH and (e) DPhHOH. Colors in parentheses correspond to the molecular color in the packing diagram in Fig. 6.



Fig. 8. Coupled C, B, A and B intermolecular interactions in crystalline (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH** and (d) **DPhc-HexOH**, respectively.



Fig. 9. Coupled B (lower), C (upper left) and D (upper right) intermolecular interactions in DPhHOH.



Fig. 10. Aggregate formation by hydrogen bonding in **DPhHOH**.



Fig. 11. T_n states related to ISC in (a) **DPhMeOH**, (b) **DPhEtOH**, (c) **DPhc-PrOH** and (d) **DPhc-HexOH**.

ounderegio