

Enhancement of Phosphorescence and Unimolecular Behavior in the Solid State by Perfect Insulation of Platinum–Acetylide Polymers

Hiroshi Masai,[†] Jun Terao,^{*,†} Satoshi Makuta,[‡] Yasuhiro Tachibana,^{*,‡} Tetsuaki Fujihara,[†] and Yasushi Tsuji[†]

[†]Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

[‡]School of Aerospace, Mechanical and Manufacturing Engineering, RMIT University, Bundoora, Australia

Supporting Information

ABSTRACT: Controlling the thermal fluctuations and molecular environment of a phosphorescent polymer backbone is vital to enhancing its phosphorescence intensity in the solid state. Here, we demonstrate enhanced phosphorescence control through a systematic investigation of cyclodextrin-based insulated platinum–acetylide polymers with well-defined coverage areas. Modification of the coverage areas revealed two unprecedented effects of macrocyclic insulation on phosphorescence behavior. First, the insulation of particular areas suppresses the thermal relaxation processes of the triplet species because of the restriction of structural fluctuations. Cyclic insulation fixes a polymer chain and concomitantly enhances the phosphorescence intensity in both the solution and solid states. Second, complete three-dimensional insulation protects the polymer from interactions with other platinum and acetylide units, and even oxygen molecules. Notably, these polymers display identical phosphorescence behaviors in both the solution and solid states, essentially achieving “unimolecular phosphorescence.”

Transition-metal complexes have gained importance as components for light-emitting diodes (LEDs)¹ and in optical sensing² and bioimaging³ devices because of their highly effective and long-wavelength phosphorescence at room temperature. In the solid state, they are expected to produce higher-density phosphorescent materials, which will display brighter emissions-per-unit-volume than their dilute counterparts. However, their desirable phosphorescence in the solid state decreases or changes drastically⁴ as a result of their indiscriminate molecular interactions with adjacent molecules.⁵ Therefore, they exhibit high performance only under highly dilute conditions (such as in a matrix with a very low doping concentration). Several examples of exceptional solid-state phosphorescence have been achieved through the adequate control of molecular arrangements or the inhibition of undesirable molecular interactions in crystalline systems.^{6,7} However, the simple concentration of diluted phosphorescent materials cannot increase their emission densities but, rather, can lead to unpredictable changes in emission behavior.⁸

As practical device materials, polymers are of interest owing to their high processability and thermodynamic stability as compared with low-molecular-weight materials. However, their

intrinsic disorder in the solid state, which is due to their high degrees of freedom, makes it difficult to organize a well-ordered structure, such as in the crystalline solid state. For this reason, applications of phosphorescent polymer materials have been limited to highly diluted systems, which are usually formed by doping a polymer matrix or through copolymerization with a low mixing ratio.⁹ Thus, to achieve high-density phosphorescence in polymer solid materials, two contradictory requirements must be simultaneously satisfied: (i) a higher concentration for brighter emission and (ii) a lower concentration to inhibit molecular interactions. Nevertheless, because of their potential application in solid-state phosphorescent polymer devices, the development of such materials has been eagerly pursued; the insights obtained would contribute to progress in the field of device science.

In 2005, Schanze et al. reported a Pt–acetylide polymer in which bulky iptycene side chains were used to suppress molecular interactions and enhance phosphorescence in the solid state.¹⁰ This concept motivated us to establish a general insulation strategy for a phosphorescent polymer, to optimize the emission behavior in the solid state. Herein, we systematically investigate insulated solid-state phosphorescent polymers. By using macrocycles for higher-order inhibition, only the desired area of a polymer chain can be covered, without any interstitial space, to achieve higher-density phosphorescence. During our study on the synthesis of a 3-D insulated conjugated polymer, poly(phenylene ethynylene) (polyPE), covered with permethylated α -cyclodextrin (PM α -CD) macrocycles,¹¹ we developed omnidirectionally insulated metallopolymers composed of Pt–acetylide and oligoPE as the polymer backbone.¹² In this study, we systematically designed and synthesized various omnidirectionally insulated polymers with different coverage ratios and areas. Two unprecedented cyclic insulation effects on the phosphorescence behavior of the metallopolymers will be described: (i) the cyclic insulation enhances phosphorescence; and (ii) identical phosphorescence behaviors are observed in the high-density solid state as well as in dilute solution.

Monomer **1** was synthesized in three steps from the PM α -CD monotosylate (Scheme 1).^{11a} Then, **1** was converted to insulated complex **2** through hydrophilic–hydrophobic interactions in MeOH/H₂O (2:1). Under the same solvent conditions, the intermediate pseudorotaxane structure of **2** was fixed by expanding the oligoPE unit through Sonogashira coupling with

Received: August 21, 2014

Published: October 2, 2014

Scheme 1. Synthetic Route for Polymers 4–6

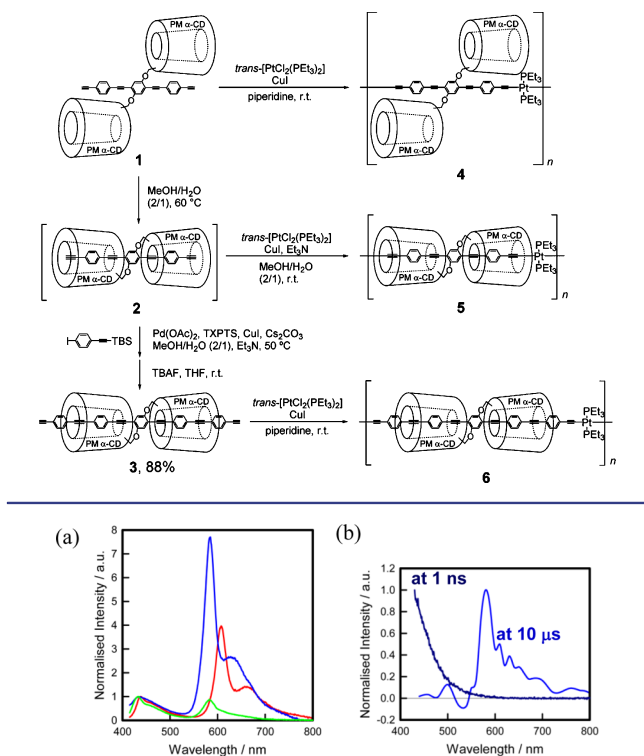


Figure 1. (a) Normalized emission spectra (excitation: 405 nm) of 4 (red), 5 (blue), and 6 (green) in CHCl₃ under N₂ atmosphere. (b) Normalized transient emission spectra of 5 in CHCl₃ under N₂ atmosphere at 1 ns and 10 μs after excitation at 405 nm.

tert-butyldimethylsilyl (TBS)-protected *p*-iodophenylacetylene in the presence of tris(4,6-dimethyl-3-sulfanato)phenyl phosphine trisodium salt (TXPTS) as a water-soluble phosphine ligand, followed by deprotection of the TBS groups to form the fixed insulated conjugated monomer 3.^{11c} The uninsulated Pt-acetylide polymer 4 was synthesized by Cu-catalyzed transmetalation of 1 with *trans*-PtCl₂(PEt₃)₂ in a hydrophobic solvent (piperidine).¹² The corresponding insulated polymer 5 was obtained from the same monomers in the hydrophilic solvent, MeOH/H₂O (2:1), from insulated complex 2. In this study, to examine the effects of the cyclic insulation area and PE units, insulated polymer 6 was synthesized from 3 bearing different oligoPE units.^{13,14}

We first compared the phosphorescence emission spectra of polymers 4–6 in degassed dilute CHCl₃ (Figure 1a).¹⁵ 5 shows emission maxima at 433 and 585 nm. The transient emission spectra obtained at 1 ns and 10 μs (Figure 1b) indicate that the shorter-wavelength emission can be attributed to fluorescence. In contrast, the long-wavelength emission accompanying the clear vibration band can be identified as phosphorescence.^{10,16} Similarly, 4 shows fluorescence at 438 nm and phosphorescence at 608 nm in CHCl₃. The emissions of insulated polymers 5 and 6 are blue-shifted compared with those of the uninsulated polymer 4 because of the fixation of the twisted conformation of the oligoPE units by encapsulation, which shortens the effective conjugated length of the oligoPE units of 5 and 6.^{11a,17} The phosphorescence intensity of 6 is considerably lower than those of 4 and 5 owing to a decrease in spin–orbit coupling with the decreasing content of Pt-acetylide units per polymer segment (Figure S4). Interestingly, insulated polymer 5 displays stronger

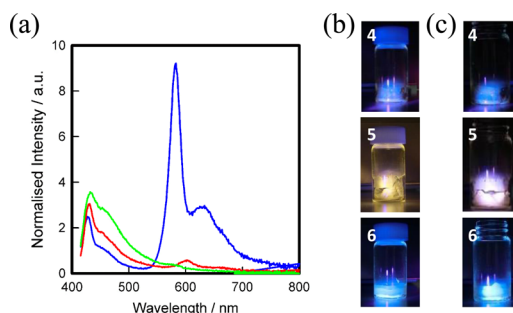


Figure 2. (a) Emission spectra of polymer solids of 4 (red), 5 (blue), and 6 (green) under degassed conditions (excitation: 405 nm). Emission behavior of Pt-acetylide polymer solids of 4–6 under (b) N₂ and (c) air (excitation: 380–425 nm).

phosphorescence and a 2-fold-higher quantum yield than its uninsulated counterpart 4 (5: 5.4% vs 4: 2.3%), indicating that the cyclic insulation for the Pt-acetylide backbones is essential for the notable enhancements in 5. The cyclic insulation of 5 provides high rotational and bending barriers to the polymer backbone, which prohibits structural fluctuations under ambient conditions.¹⁷ It is generally difficult to inhibit the molecular fluctuations of benzene rings adjacent to oligoPE units with conventional protectants such as dendrons and macrocycles (Figure S5). In contrast, our [1]rotaxane structures successfully fix the oligoPE units in 5 by insulation and linkages. Such 3-D restraint for 5 efficiently enhances its phosphorescence through the peculiar effects of linked rotaxane structures.

In order to assess the potential for protection against oxygen, a typical phosphorescence quencher, we measured the transient emission decays of dilute solutions of 4 and 5 (Figure S6a). Under deoxygenated conditions, the transient emission decay fittings of 4 and 5 in Figure S6a show the same lifetime (30 μs). In contrast, under an air atmosphere, the lifetime of 5 (10 μs) is ~15 times longer than that of 4 (0.65 μs). This difference clearly indicates that the insulation of 5 extends the phosphorescence lifetime by inhibiting interactions with oxygen. These results demonstrate the isolation of insulated polymer 5 from the external environment because of its 3-D covering.¹⁸

We next investigated the effect of insulation in the solid state. Triplet-based phosphorescence is subject to quenching via molecular interactions in the solid state, since the triplet-state lifetime is generally longer than that of the singlet state.^{19,20} Amorphous films were prepared by evaporating a polymer solution in CHCl₃ on a glass substrate without annealing. Figure 2a shows the photoluminescence spectra of polymer solids 4–6 under degassed conditions.²¹ As expected, insulated polymer 5 displays a strong orange emission. In contrast, the corresponding uninsulated polymer 4, which exhibited phosphorescence in dilute solution, shows very weak phosphorescence in the solid state, despite its bulky PM α-CD side chains which cover the polymer backbone. These results indicate that the insulation in polymer 5 prevents interactions with adjacent molecules, even in the solid state, achieving high-density phosphorescence. Because 5 also tolerated oxygen, as described above, it even exhibits phosphorescence in the solid state under an air atmosphere (Figures 2c and S3). In contrast, despite its insulation, 6 does not show phosphorescence in the solid state, but only fluorescence. We postulate that the triplet-state quenching observed in the polymer 6 solid is caused by intermolecular interactions, similar to the case of 4, because 6 also displayed phosphorescence in dilute solution.

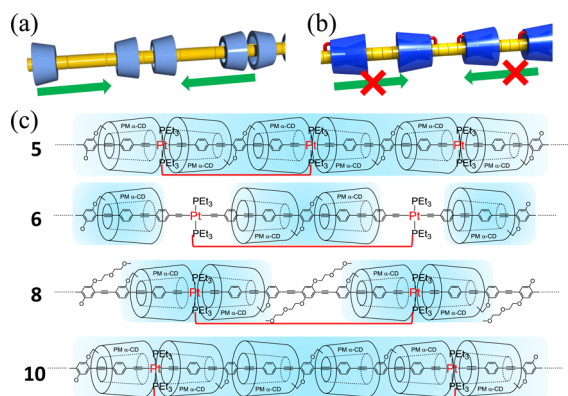


Figure 3. Comparison of the potential for shuttling between (a) conventional and (b) our linked rotaxanes. (c) Illustration of the coverage ratios and areas of insulation for polymers 5, 6, 8, and 10. Red lines show the repeating units of the polymers.

5 showed both phosphorescence and fluorescence, whereas 6 showed only fluorescence, although they are both insulated polymers. To investigate the intermolecular interactions in detail, we focused on the three structural differences between these two insulated polymers: (i) 5 has a higher coverage ratio over its backbone than 6; (ii) the Pt complex area in 5 is covered but that in 6 is not; and (iii) the oligoPE unit in 5 is shorter than that in 6.²² Our synthetic method for insulated metallopolymers bearing the poly[1]rotaxane structure allows the synthesis of individual well-defined polymers insulated in targeted areas at desired coverage ratios with the PE units, since the linkages between the conjugated axles and macrocycles of the rotaxanes prevent the shuttling of cycles that occurs in conventional rotaxanes (Figure 3a and 3b). To investigate the relationship between phosphorescence and the insulated sites in the oligoPE units, we synthesized 8 (Scheme S5), having different coverage positions than 6. Polymer 8 contains oligoPE units of the same length as in 6, and the same number of PM α -CDs in its repeating units. Yet, in 8, the areas near platinum are covered, whereas, in 6, the centers of the PE units are covered, albeit in the same ratio (Figure 3c). Polymer 8 was synthesized by the sequential self-inclusion of 7 followed by Cu-catalyzed transmetalation with the Pt complex in a hydrophilic solvent.¹⁴

In the solid state, 8 exhibited only fluorescence emission, whereas it displayed phosphorescence in CHCl_3 , similarly to 6. This indicates the failure of 8 to inhibit intermolecular interactions (Figure 4).²¹ This result shows that solid-state phosphorescence is not affected by the location of the insulation in the main chain but, rather, by the other two factors: the coverage ratio or conjugation length. A completely insulated polymer, 10, bearing expanded oligoPE units covered by four PM α -CDs, was synthesized from monomer 9.¹⁴ 10 displayed phosphorescence emission in the solid state (Figure 4). These results suggest that the triplet-state quenching of 6 and 8 was not related to the longer conjugation lengths compared with that of 5 and demonstrate that a high coverage ratio of the polymer backbone is essential to obtain high phosphorescence intensity in the solid state and that the phosphorescence of 4, 6, and 8 is quenched in the solid state because of their low coverage ratios.

To rationalize the origin of quenching by interactions, we performed density functional theory (DFT) calculations for the partial structure 11 of 6 and 8 (Figure 5a). The singly occupied molecular orbital (SOMO) had predominantly lowest unoccupied molecular orbital (LUMO) characteristics, fully spread over

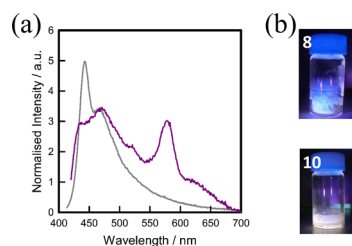


Figure 4. (a) Emission spectra of polymer solids 8 (gray) and 10 (dark pink) under degassed conditions (excitation: 405 nm). (b) Emission behavior of polymer solids 8 and 10 under N_2 (excitation: 380–425 nm).

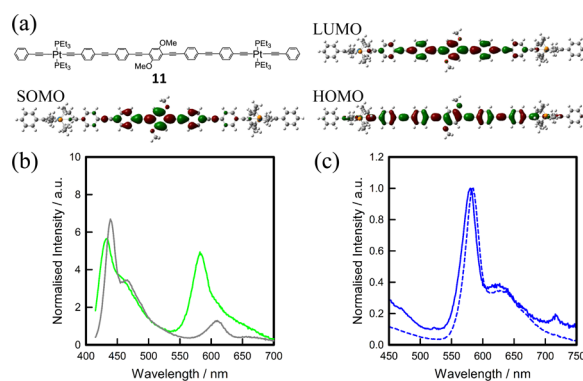


Figure 5. (a) Optimized molecular structures and frontier orbitals of partial structure 11, calculated using DFT. Normalized emission spectra of (b) dilute CHCl_3 solutions of 6 (green) and 8 (gray), and (c) insulated polymer 5 in dilute CHCl_3 solution (dashed) and in the solid state (solid), under degassed conditions.

the oligoPE, and the highest occupied molecular orbital (HOMO) was delocalized across the main axle. Phosphorescence in Pt-acetylide polymers with oligoPEs is known to be dominated by π - π^* transitions in the PE units,²³ which is also supported by the clear vibration bands in the emission spectra, as mentioned. The π -orbitals in the steady and excited states of polymers 6 and 8 in the solid state can be exposed to adjacent polymers, which results in multimeric species and destabilizes their excited forms. In contrast, in fully insulated 5 and 10, the π -orbitals are protected, disrupting interactions with nearby polymers in the solid state. Moreover, the excited molecular orbitals of 11, especially the SOMO, are focused at the center of the PE unit rather than near the Pt complexes. The location of the orbital distribution would strongly affect the phosphorescence intensity of the partially insulated polymers 6 and 8, which differ only in their coverage areas. The cyclic insulation of 6 on the PE centers results in stronger phosphorescence in dilute CHCl_3 solution than that of 8 near the Pt complexes (Figure 5b).²¹ This difference in the insulation area is probably derived from the cyclic restraint of the thermal relaxation process. As mentioned above, the fixation of molecular motions and rotations would protect the triplet species. The π - π^* -transition-based phosphorescence of 6 was efficiently stabilized by covering the center of the π -conjugation. An enhancement in the phosphorescence from 6 was also observed in the solid state compared with that in 8 (Figure S11).

Finally, to quantitatively evaluate the insulating effect of 5, we compared the emission wavelengths and quantum yields between a dilute solution and the solid state. Almost identical emission spectra were obtained under deoxygenated conditions in solution ($\lambda_{\text{max}} = 585 \text{ nm}$) and the solid state ($\lambda_{\text{max}} = 581 \text{ nm}$) (Figure 5c).

Likewise, the quantum yields were nearly identical in solution (5.4%) and the solid state (4.4%). This is the first demonstration of nearly equal phosphorescence emission behaviors in dilute-solution and high-density-solid states. These results suggest that the complete insulation of phosphorescent polymers realizes “unimolecular phosphorescence,” even in the solid state.

In conclusion, higher-order inclusion effects were observed on the phosphorescence behavior of Pt-acetylide polymers fully covered with PM α -CDs. To our knowledge, this is an unprecedented example which integrates the features of phosphorescence and rotaxane structure.²⁴ Systematic syntheses of targeted-coverage polymers distinguished two cyclic insulation effects that stabilized the intermediate triplet species, which are sensitive to interactions with neighboring molecules. First, the targeted insulation for π -conjugated areas efficiently enhanced the phosphorescence intensity in both the solution and solid states owing to the restriction of structural fluctuations. Second, complete 3-D insulation generated almost identical phosphorescence emission behaviors in solid systems as in dilute solutions because of protection from all interactions. Moreover, such insulation also led to oxygen tolerance: phosphorescence was observed under air in the solid state. This is the first example of the unimolecular phosphorescence of a polymer material in the high-density solid state. These results, derived from the linked rotaxane structures, indicate that even triplet species can be enhanced and stabilized by the appropriate molecular design and can guide the development of solid-state molecular devices.

■ ASSOCIATED CONTENT

Supporting Information

Detailed synthetic procedures, chromatogram, and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

terao@scl.kyoto-u.ac.jp

yasuhiro.tachibana@rmit.edu.au

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Funding Program for JSPS Research Fellow and Grant-in-Aid for Scientific Research on Innovative Areas (“Molecular Architectonics” and “Soft Molecular Systems”) from MEXT, Japan.

■ REFERENCES

- (1) (a) Costa, R. D.; Orti, E.; Bolink, H. J.; Monti, F.; Accorsi, G.; Armaroli, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 8178. (b) Evans, R. C.; Douglas, P.; Winscom, C. J. *Coord. Chem. Rev.* **2006**, *250*, 2093. (c) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. *Adv. Mater.* **2011**, *23*, 926.
- (2) (a) Ma, D.-L.; Ma, V. P.-Y.; Chan, D. S.-H.; Leung, K.-H.; He, H.-Z.; Leung, C.-H. *Coord. Chem. Rev.* **2012**, *256*, 3087. (b) Liu, Z.; He, W.; Guo, Z. *Chem. Soc. Rev.* **2013**, *42*, 1568.
- (3) (a) Mou, X.; Wu, Y.; Liu, S.; Shi, M.; Liu, X.; Wang, C.; Sun, S.; Zhao, Q.; Zhou, X.; Huang, W. *J. Mater. Chem.* **2011**, *21*, 13951. (b) Baggaley, E.; Weinstein, J. A.; Williams, J. A. G. *Coord. Chem. Rev.* **2012**, *256*, 1762.
- (4) (a) Zhu, Y.-C.; Zhou, L.; Li, H.-Y.; Xu, Q.-L.; Teng, M.-Y.; Zheng, Y.-X.; Zuo, J.-L.; Zhang, H.-J.; You, X.-Z. *Adv. Mater.* **2011**, *23*, 4041. (b) Juliá, F.; Bautista, D.; Fernández-Hernández, J. M.; González-Herrero, P. *Chem. Sci.* **2014**, *5*, 1875.

(5) Triplet-triplet annihilations are proposed as thermal relaxation processes of excited species; Wagner, P. J.; Hammond, G. S. *Adv. Photochem.*, Vol. 5; Noyes, W. A., Jr.; Hammond, G. S.; Pitts, J. N., Jr., Eds.; Interscience Publishers: New York, 1968; p 21.

(6) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361.

(7) (a) Komiya, N.; Okada, M.; Fukumoto, K.; Jomori, D.; Naota, T. *J. Am. Chem. Soc.* **2011**, *133*, 6493. (b) Bolton, O.; Lee, K.; Kim, H.-J.; Lin, K. Y.; Kim, J. *Nat. Chem.* **2011**, *3*, 205.

(8) Rare dendric protections have contributed to the same emission behaviors in the solution and solid: (a) Lo, S.-C.; Harding, R. E.; Shipley, C. P.; Stevenson, S. G.; Burn, P. L.; Samuel, I. D. W. *J. Am. Chem. Soc.* **2009**, *131*, 16681. Most dendritic examples change the wavelength and/or quantum yield of phosphorescence according to their concentration: (b) Lo, S.-C.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Sammel, I. D. W. *Adv. Mater.* **2002**, *14*, 975. (c) Kim, J. J.; You, Y.; Park, Y.-S.; Kim, J.-J.; Park, S. Y. *J. Mater. Chem.* **2009**, *19*, 8347. (d) Tang, M.-C.; Tsang, D. P.-K.; Chan, M. M.-Y.; Wong, K. M.-C.; Yam, V. W.-W. *Angew. Chem., Int. Ed.* **2013**, *52*, 446.

(9) Gong, S.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2012**, *41*, 4797.

(10) Zhao, X.; Cardolaccia, T.; Farley, R. T.; Abboud, K. A.; Schanze, K. S. *Inorg. Chem.* **2005**, *44*, 2619.

(11) (a) Terao, J.; Tsuda, S.; Tanaka, Y.; Okoshi, K.; Fujihara, T.; Tsuji, Y.; Kambe, N. *J. Am. Chem. Soc.* **2009**, *131*, 16004. (b) Terao, J.; Wadahama, A.; Matono, A.; Tada, T.; Watanabe, S.; Seki, S.; Fujihara, T.; Tsuji, Y. *Nat. Commun.* **2013**, *4*, 1691. (c) Terao, J.; Homma, K.; Konoshima, Y.; Imoto, R.; Masai, H.; Matsuda, W.; Seki, S.; Fujihara, T.; Tsuji, Y. *Chem. Commun.* **2014**, *50*, 658. (d) Recent reviews: Terao, J. *Polym. Chem.* **2011**, *2*, 2444.

(12) Terao, J.; Masai, H.; Fujihara, T.; Tsuji, Y. *Chem. Lett.* **2012**, *41*, 652.

(13) The ³¹P NMR spectra of all polymers indicating that the polymers have a *trans*-Pt(PEt₃)₂ coordination geometry: Ohshiro, N.; Takei, F.; Onitsuka, K.; Takahashi, S. *J. Organomet. Chem.* **1998**, *569*, 195.

(14) The chemical shifts of the PEt₃ protons in the ¹H NMR spectra of polymers **5**, **8**, and **10** in CDCl₃ (1.99–2.01 ppm) were clearly shifted upfield compared with those for **4** and **6** (2.17 ppm), since the former protons existed near the Me groups of the outer-ring lip of PM α -CD.

(15) (a) Wong, W.-Y.; Liu, L.; Poon, S.-Y.; Choi, K.-H.; Cheah, K.-W.; Shi, J.-X. *Macromolecules* **2004**, *37*, 4496. (b) Haskins-Glusac, K.; Pinto, M. R.; Tan, C.; Schanze, K. S. *J. Am. Chem. Soc.* **2004**, *126*, 14964.

(16) Wittmann, H. F.; Friend, R. H.; Khan, M. S.; Lewis, J. J. *Chem. Phys.* **1994**, *101*, 2693.

(17) Kiguchi, M.; Nakashima, S.; Tada, T.; Watanabe, S.; Tsuda, S.; Tsuji, Y.; Terao, J. *Small* **2012**, *8*, 726.

(18) The lifetimes of triplet species had a large difference between **5** (30 μ s) and **4** (10 μ s) in a nitrogen atmosphere, suggesting that the insulation of **5** also prohibited triplet quenching processes other than that by oxygen, possibly such as molecular motion (Figure S6b).

(19) The singlet-based fluorescence of conjugated molecules did not decay dramatically even in the solid state with a certain level of insulation: Terao, J.; Ikai, K.; Kambe, N.; Seki, S.; Saeki, A.; Ohkoshi, K.; Fujihara, T.; Tsuji, Y. *Chem. Commun.* **2011**, *47*, 6816.

(20) Many solid-state fluorescent polymers bearing protection have been reported: (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864. (b) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658. (c) Pan, C.; Sugiyasu, K.; Wakayama, Y.; Sato, A.; Takeuchi, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 10775.

(21) The spectra were corrected to the same number of photons absorbed at the excitation wavelength.

(22) (a) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Köhler, A.; Friend, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 9412. (b) Silverman, E. E.; Cardolaccia, T.; Zhao, X.; Kim, K.-K.; Haskins-Glusac, K.; Schanze, K. S. *Coord. Chem. Rev.* **2005**, *249*, 1491.

(23) Köhler, A.; Wilson, J. S.; Friend, R. H.; Al-Suti, M. K.; Khan, M. S.; Gerhard, A.; Bäessler, H. *J. Chem. Phys.* **2002**, *116*, 9457.

(24) (a) Liang, A.-H.; Zhang, K.; Zhang, J.; Huang, F.; Zhu, X.-H.; Cao, Y. *Chem. Mater.* **2013**, *25*, 1013. (b) Cao, J.; Ma, X.; Min, M.; Cao, T.; Wu, S.; Tian, H. *Chem. Commun.* **2014**, *50*, 3224.