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COMMUNICATION

A room-temperature phosphorescent polymer film containing a molecular web based on one-dimensional chiral stacking of a simple luminophore†

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We propose a new approach for a totally organic, room-temperature phosphorescent system with a lifetime on the order of milliseconds, which is achieved by promotion of the one-dimensional chiral stacking of a simple, small fluorophore in a solution state. The versatility of this system is highlighted by its good applicability to the fabrication of a phosphorescent polymer film. This paper demonstrates the first example of a room-temperature phosphorescent polymer film prepared with our methodology.

Room-temperature phosphorescence (RTP) is an attractive technique in various research fields, and has been used for optical applications¹, solar cells², oxygen probes in cells³, and luminescent sensors for identification of chemical substances⁴. Most reported RTP materials are organometallic compounds that contain rare-metals⁵, which result in a heavy metal effect, and complicated organic materials with sterically bulky substituents. Moreover, there are few solution-based RTP systems.⁶ Therefore, a new RTP system composed of a simple and purely organic compound in solution is desired. This new type of RTP system would have the distinct advantages of high applicability in a normal-pressure wet process, easy synthesis, easy handling and low cost.

This paper proposes a new approach to solution-state RTP that is applicable to a phosphorescent polymer system. Our proposed RTP system is based on one-dimensional chiral stacking of a simple luminophore in solution and the formation of a phosphorescent molecular web in a polymer (Fig. 1). For this purpose, a planar benzothiophene (BT) derivative with a large dipole moment was selected as a candidate luminophore. The BT derivative was functionalised with a chiral molecular tool (G) to promote three-dimensional network formation of its one-dimensional aggregates. This

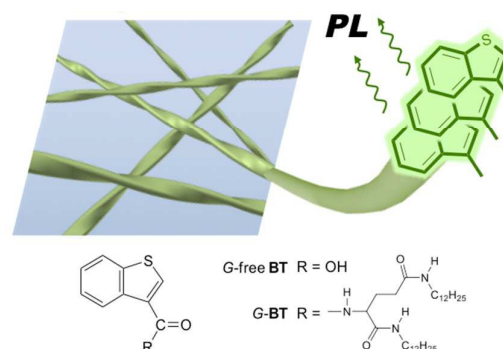


Fig. 1 Schematic illustration on our conceptual approach for the phosphorescent molecular web in solution and polymer. In our approach, the molecular web can be produced through one-dimensional stacking of a benzothiophene derivative as a simple, planar luminophore for solution and polymer systems. PL: Phosphorescence. The chemical structures are the benzothiophene derivatives used in this study.

method has several advantages: (1) no sterically bulky substituents are needed in the molecular design of the luminophore, which makes the molecular design more flexible. (2) Enhanced phosphorescence intensity is achieved through molecular stacking as a result of effective suppression of molecular vibration. This is essential for RTP in solution because it reduces the consumption of the excitation energy through thermal processes.^{6a} (3) The large dipole moment in a planar luminophore suppresses *H*-aggregation, which causes luminescence quenching, and induces *J*-aggregation, which enhances the luminescence.⁷ (4) Our solution-state RTP system supports a normal-pressure wet fabrication process for transparent optical materials by promoting one-dimensional aggregation of the luminophore over three-dimensional growth, which causes strong light scattering.

In this paper, we demonstrate a new solution-state RTP system using a BT derivative functionalised with a tool for promoting one-dimensional aggregation (G, Fig. 2). We also describe the fabrication of a functional transparent polymer film containing a webbed phosphorescent network in its RTP system.

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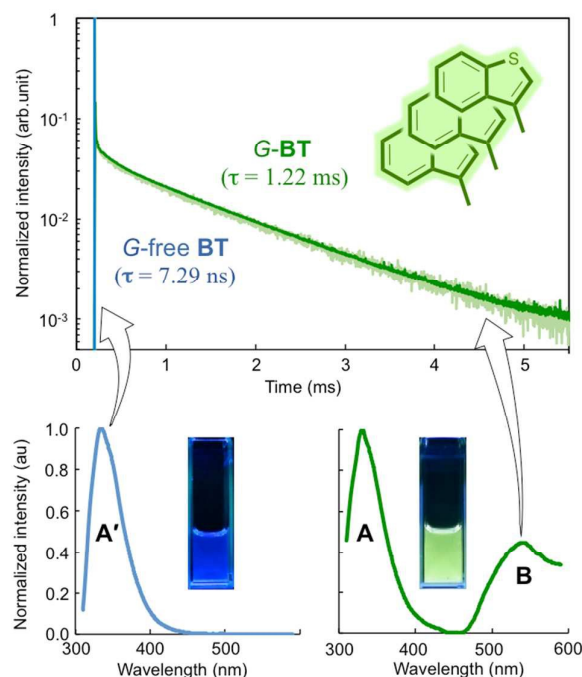


Fig. 2 Luminescence decay curves and fluorescence spectra of *G*-free **BT** and *G*-**BT** (0.15 mM) in methylcyclohexane at 298 K. The fluorescence spectra and the luminescence decay curves were obtained by irradiation at 300 and 280 nm, respectively. The solid dark green line shows the fitting curve.

G-Free **BT** (ESI⁺) and *G*-functionalised **BT** (*G*-**BT**) (ESI⁺) showed good solubility in various organic solvents. Clear solutions were obtained when *G*-free **BT** and *G*-**BT** were dispersed at 0.15 mM in methanol, ethanol, THF, chloroform, toluene, and methylcyclohexane. However, the luminescent colours of the *G*-free **BT** and *G*-**BT** solutions in methylcyclohexane at room temperature (298 K) were completely different from each other when they were excited at 300 nm (Fig. 2). This wavelength corresponds to the maximum of the absorption band of a benzothiophene moiety.

The difference in the luminescence colours can be clearly understood from the fluorescence spectra of the two compounds, shown in Fig. 2. The spectrum of *G*-**BT** exhibits two peaks at 330 (species **A**) and 537 nm (species **B**), whereas that of *G*-free **BT** contains a single peak at 334 nm (species **A'**). The Stokes shift was as large as 237 nm in species **B**. In addition, we found that the longest-lived component of the fluorescence lifetime (τ) was of the millisecond order ($\tau = 1.22$ ms) for species **B**, but remained on the order of nanoseconds ($\tau = 7.12$ ns) for species **A** (Fig. S1) (ESI⁺). (The decay curves in Figs. 2 and S1 include decays based on the excitation light-scattering.) To understand this considerable difference, the dispersion state of *G*-**BT** was further investigated.

The aggregation morphology was investigated. The confocal microscopy image (Fig. 3a) shows that *G*-**BT** was dispersed as fluorescent fibrils with lengths of more than 10 μm . The diameters (thicknesses) of the fibrils were determined using transmission electron microscopy (TEM), and were a minimum of 10 nm, which corresponds to several times larger than the molecular length of *G*-**BT**. In contrast, no aggregates were

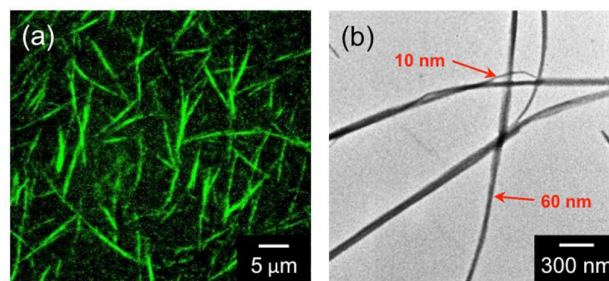


Fig. 3 (a) Fluorescence confocal microscopy image of a methylcyclohexane solution of *G*-**BT** (0.15 mM, excitation at 488 nm, observation at 520–600 nm, and modification with noise reduction). (b) TEM image obtained from the *G*-**BT** solution (0.15 mM) after staining with uranyl acetate. [As complementary results of the confocal microscopy, luminescence of *G*-**BT** in methylcyclohexane was observed under UV and blue light excitation, as shown for details in Fig. S2 and the experimental section of ESI⁺.]

observed in chloroform, which is a good solvent for *G*-**BT**. From these observations, we conclude that *G*-**BT** is dispersed in non-polar solvents such as methylcyclohexane as fibrillar aggregates with nano-sized diameters. The resultant solution appears to be transparent because of the low light-scattering ability of these aggregates.

The fluorescence lifetime (τ) was further investigated. As summarised in Table 1, *G*-free **BT** exhibited a nanosecond-order lifetime ($\tau = 7.29$ ns at 334 nm), which is almost equal to that of species **A** in *G*-**BT**. These values correspond to those of molecular luminophores.⁸ Therefore, species **A** in *G*-**BT** can be attributed to the monomeric dispersion state. In contrast, τ reached 1.22 ms for species **B**. A similarly long τ was observed in the non-polar solvent cyclohexane. However, when trifluoroacetic acid (TFA) was added to solutions of *G*-**BT** in non-polar solvents to inhibit molecular aggregation, species **B** disappeared (Fig. S3) (ESI⁺) and this was accompanied by a remarkable decrease in τ to a value similar to that of the monomer (Table 1). A similar effect was observed when the concentration was reduced to 10 μM . These results indicate that the long lifetime is only achieved on aggregation of *G*-**BT**. In agreement with this hypothesis, the crystalline solid of *G*-free **BT** obtained by recrystallisation from toluene solution exhibited a large Stokes shift of 215 nm and a long lifetime ($\tau = 1.38$ ms at 515 nm), as shown in Fig. S4) (ESI⁺).

Table 1. Solvent and concentration dependence of τ in *G*-free **BT** and *G*-**BT** at 297 K.

Luminophore	Solvent		Concentration (mM)	τ^b at peak wavelength	
	Name	ϵ^a			
<i>G</i> - BT	Cyclohexane	2.02	0.15	7.72 ns	1.27 ms
				(330 nm)	(540 nm)
	Methylcyclohexane	2.07	0.15 ^c	7.12 ns	1.22 ms
				(330 nm)	(537 nm)
Methylcyclohexane	2.07	0.01	< 1 ns	none	
			(372 nm)	(330 nm)	
<i>G</i> -free BT	Methylcyclohexane	2.07	0.15	7.14 ns	none
				(330 nm)	(342 nm)
<i>G</i> -free BT	Methylcyclohexane	2.07	0.15	1.25 ns	none
				(342 nm)	(334 nm)

^a Dielectric constant. ^b The measurement was carried out by excitation at 280 nm. The peak-top wavelength in the observed luminescent band is noted in a bracket.

^c Trifluoroacetic acid (0.05 v/v%) was added to the methylcyclohexane solution.

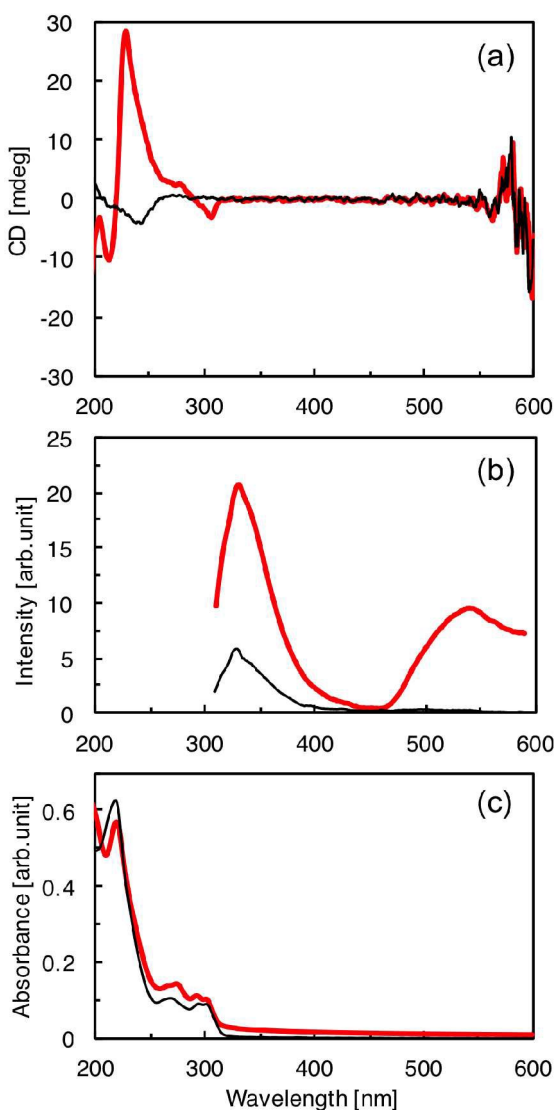


Fig. 4 Temperature dependence of (a) CD, (b) fluorescence, and (c) UV-visible spectra of *G*-BT solutions. Concentration, 0.15 mM; solvent, methylcyclohexane. The red and black lines were obtained at 298 and 363 K, respectively.

UV-visible and circular dichroism (CD) spectra were measured to obtain further information on the molecular orientation of *G*-BT. As shown in Fig. 4a, the CD spectrum at 298 K exhibited a strong Cotton effect with a positive signal around the absorption band of the BT moiety. Because the BT moiety does not contain a chiral centre and almost no CD signal was detected when the solution was heated to 363 K to promote the aggregate-to-monomer phase transition, it is likely that the CD signal observed at 298 K is due to the induction of chirality in the *G*-BT aggregates.

The CD pattern provides us with considerable information on the chiral orientation of the BT moiety. Only a positive Cotton effect was observed, which indicates R-chirality, but this effect is completely different from that observed in Davydov splitting.⁹ Therefore, the chiral orientation around the BT moiety is not based on *H*-like aggregation.^{10,11} As support for this assumption, in our system, the fluorescence intensity

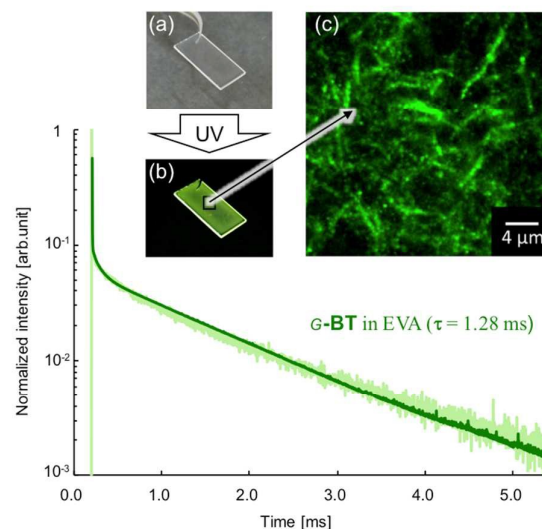


Fig. 5 Luminescence decay curves at 525 nm of a transparent poly(ethylene-co-vinyl acetate) (EVA) film containing 0.64 wt% *G*-BT prepared by a casting method on a quartz glass. The film thickness was 125 μm . The dark and light green lines indicate the observed and fitted decay curves, respectively. Photographs (a) and (b) are of the *G*-BT-containing EVA film under normal and UV light, respectively. The confocal microscopic image (c) was obtained with excitation at 488 nm and observation at 520–600 nm.

around 330 nm increased but also the phosphorescence newly appeared around 537 nm at 298 K (Fig. 4b) and a slight red shift was observed (Fig. 4c), whereas *H*-aggregation promote only fluorescence quenching. These observations allow us to conclude that the *G*-moiety plays an essential role in the phosphorescence-promoting aggregation of BT moieties in a non-polar solvent system.

In this paper, we also demonstrate the first example of the incorporation of our RTP system into a polymer film, which would expand its potential applicability in optical applications. For this purpose, a composite film was prepared by simple mixing of *G*-BT (0.64 wt% with respect to the polymer component) in a poly(ethylene-co-vinyl acetate) (EVA)-containing methylcyclohexane solution, followed by drop-casting on a quartz plate. The obtained film had a thickness of 125 μm and high transparency as shown in Fig. 5a.

To investigate the optical properties and aggregation morphology of *G*-BT in the EVA film, fluorescence spectroscopy, fluorescence lifetime, and confocal microscopy experiments were conducted. We observed two luminescence peaks at 331 and 525 nm (Fig. S54) (ESI[†]), which are similar to those in the solution system. In addition, these experiments confirmed that the luminescence of the peak at 525 nm was phosphorescence with a lifetime of 1.28 ms (Fig. 5). Furthermore, we observed luminescent aggregates in the polymer system using confocal microscopy. The observed aggregation morphology was similar to that in the solution system. These results show that the new RTP system cannot only be realised in solution, but that it is also applicable for wet processing.

In conclusion, we have established a new solution RTP system through one-dimensional aggregation of a simple benzothiophene derivative functionalised with a chiral self-assembling tool. We have also demonstrated the first example of a polymer film exhibiting RTP. These achievements were

brought about by the ability of the *G*-derivative to assist in the formation of nano-fibrillar aggregates of the luminophores with chiral stacking, in both solution and polymer systems. Our new RTP system has the potential for use in various transparent optical applications.

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