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COMMUNICATION

Covalently Linked Rotaxane Encapsulation of a Benzil Core for Consistent Organic Room-Temperature Phosphorescence Across Diverse Solvents

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Sotaro Shimada, [a] Yoichi Masui,*[a] Hiromichi V. Miyagishi, [ab] Susumu Tsuda, [c] Hiroshi Masai, [ade] and Jun Terao*[a]

We achieved room-temperature phosphorescence (RTP) of benzil, an aromatic diketone, in diverse solvents, as well as in amorphous solid states, by encapsulating the core with covalently linked cyclodextrins and introducing bulky capping moieties to effectively suppress intramolecular motions.

Phosphorescence, characterized by its long-lived emission, has attracted significant interest for applications, such as in organic electroluminescence devices[1a,b] and bioimaging.[2a,b] While the presence of oxygen typically quenches phosphorescence and is therefore undesirable for emission applications, this sensitivity can be exploited in some cases for oxygen sensing.[3a,b] Thus, phosphorescent materials present a wide range of potential applications, but a common challenge associated with them is achieving sufficiently high emission efficiency.

One possible approach is to facilitate intersystem crossing (ISC), which is often achieved by introducing heavy atoms that enhance spin-orbit coupling.[4] However, these approaches raise concerns about cost and environmental impact, motivating alternative strategies. Benzil and benzophenone are classic heavy-atom-free organic phosphors.[5a-e] In particular, benzil, an aromatic diketone, is known to show weak room-temperature phosphorescence (RTP) in carefully deoxygenated solutions,[6] due to the ISC facilitated by its adjacent carbonyl groups. However, organic phosphorescence in solution is susceptible to nonradiative deactivation through intramolecular motion because the emission lifetime is longer than fluorescence.[7] Strategies, such as cooling to liquid-nitrogen temperature,[8a,b] crystallization, amorphization to restrict intramolecular rotation,[9a-d] and embedding in polymer matrices[10a-c] can enhance phosphorescence, but suppressing intramolecular motion in solution remains challenging. In solid-state systems, homopolymers or copolymers possessing a high density of functional units, typically aromatic backbones, are regarded as promising candidates for thin-film and coating applications.[11a,b] However, in such cases, another challenge emerges: close packing of the aromatic moieties enhances π–π interactions, promoting nonradiative deactivation and reducing emission efficiency.[12]

Encapsulating an emissive unit within a well-defined cage is an effective strategy to suppress intramolecular motion and thereby reduce nonradiative decay. Rebek Jr. and co-workers demonstrated that a dimeric capsule formed via hydrogen bonding between two tetraimide units in nonpolar solvents could encapsulate benzil and exhibit RTP in mesitylene[13] (Fig. 1A, a→b). However, these hydrogen-bonded cages may dissociate in polar media, thereby limiting their broad applicability.

Here, we employ the linked rotaxane strategy previously developed by our group[14a-c] (Fig. 1B). This design suppresses shuttling in the rotaxane structure, which has been used for molecular protection,[15,16] thereby enabling precise protection of the emissive core. Furthermore, the directionality of the cyclic molecule can be restricted to a single direction.[17] First, we synthesized a non-encapsulated structure **X-unenc** (a) in which a benzil core was covalently linked to two permethylated α-cyclodextrins (PM α-CDs), which are known to be soluble in a wide range of solvents. Heating this construct in polar solvents such as MeOH/H_2O induced a transformation into an encapsulated pseudo-rotaxane **X-enc** (b). For covering a wider range compared to that when using one CD, two CDs were used, which were linked to benzil for precise protection. As a result, **X-enc** is expected to exhibit RTP in solvents. However, the conversion between **X-unenc** and **X-enc** is known to be reversible,[17] with **X-enc** slowly reverting to **X-unenc** in nonpolar solvents owing to the influence of solvent polarity. Subsequent end capping with bulky stopper molecules via click reaction yields the permanently locked encapsulated structure **X-enc-cap** (c). This design ensures that high solubility is maintained in

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[a] Graduate School of Arts and Sciences, The University of Tokyo
3-8-1, Komaba, Meguro-ku, Tokyo, 153-8902 Japan
E-mail: cterao@g.ecc.u-tokyo.ac.jp
[b] (Current affiliation) Department of Chemistry, Faculty of Science, Hokkaido University, Kita-10 Nishi-8 Kita-ku, Sapporo 060-0810, Japan
[c] Department of Chemistry, Osaka Dental University
Hirakata, Osaka 573–1121, Japan
[d] (Current affiliation) Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo,
7-3-1, Hongo, Bonkyo-ku, Tokyo, 113-8654, Japan
[e] PRESTO, Japan Science and Technology Agency
4-1-8, Honcho, Kawaguchi, Saitama, 332-0012 Japan

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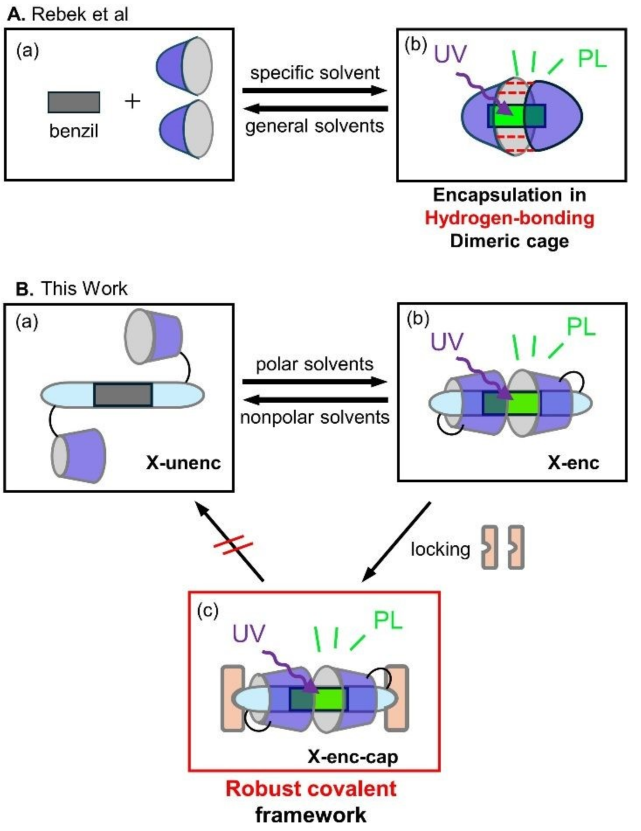

Figure 1. Methods of realizing organic RTP in A) previous work and B) this work. (a: unencapsulated structure, b: encapsulated structure without capping, c: encapsulated structure with capping)

diverse solvents while the encapsulated state of the benzil core is firmly preserved, thereby enabling phosphorescence in multiple solvents. Furthermore, we extended this strategy to polymers via alternating copolymerization with a diazide linker, yielding phosphorescent materials in which each emissive unit was appropriately and permanently encapsulated. Therefore, this linked rotaxane approach provides a rational design concept for suppressing intramolecular motion, offering a promising pathway to organic RTP in both molecular and polymeric systems.

As an initial step, **3-enc** and **3-unenc** were selected to examine the effect of the rotaxane-type encapsulation on benzil phosphorescence (Fig. 2a). Compound **1** was synthesized according to the literature.[18] Sonogashira coupling of 4,4'-dibromobenzil and **1** yielded **2**, and subsequent deprotection of the *tert*-butyldimethylsilyl (TBS) groups yielded **A**. We have previously found that linked rotaxane materials initially exist in the unencapsulated state when synthesized in less polar solvents, and convert to the encapsulated state as a thermodynamically stable form upon heating in polar solvents.[17] Accordingly, encapsulation was attempted by heating **A** in MeOH/H_2O at 60 °C for 3 h, affording **C**. ^1H nuclear magnetic resonance (NMR) spectroscopy in $CDCl_3$ (Fig. 2b) confirmed that **A** consisted of a single component, identified as **3-unenc**. In contrast, the spectrum of **C** indicated that **3-unenc** had completely disappeared, and the product was composed entirely of **3-enc**. Downfield shifts of the aromatic protons in **3-enc** compared with **3-unenc** suggested the progress of the encapsulation.[19] When the encapsulation was carried out in pure MeOH, a less polar condition, the product **B** was composed

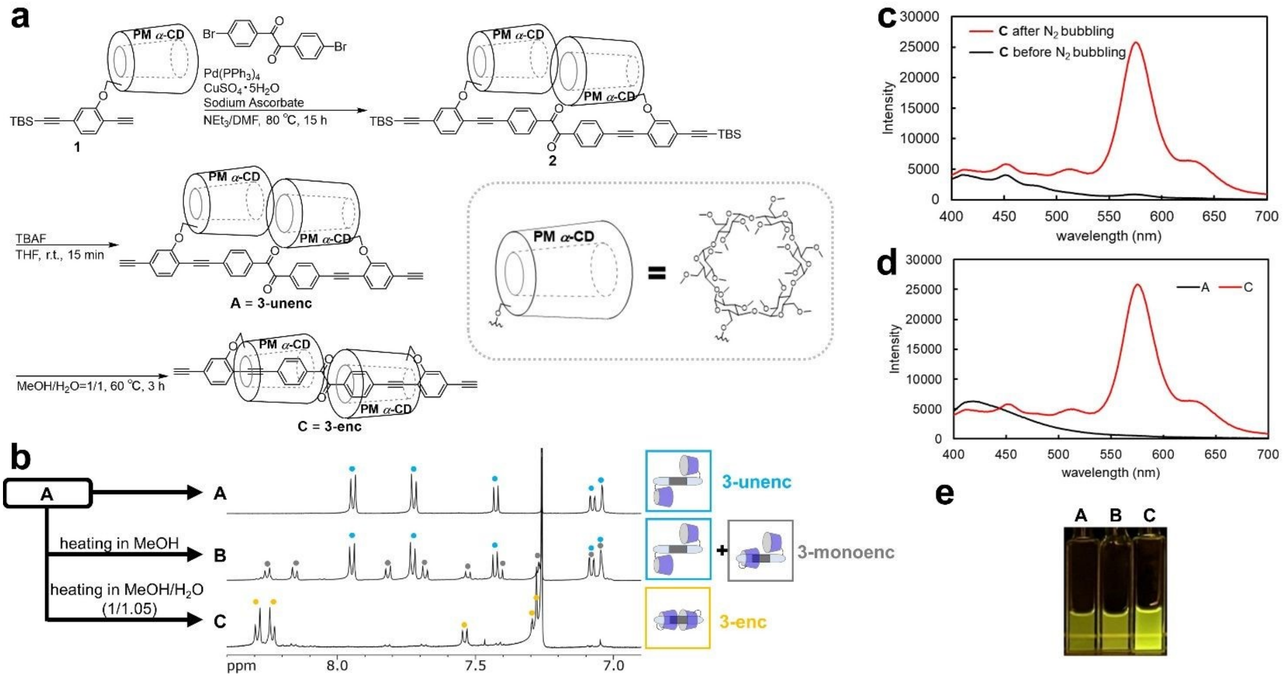

Figure 2. a) Synthetic procedure of **3-unenc** and **3-enc** b) Synthetic procedure, ^1H NMR spectra in $CDCl_3$ and inferred structures of **A**, **B** and **C** c) Emission spectra of **C** in methanol before and after nitrogen bubbling (concentration: 1×10^{-5} mol/L, excitation: 365 nm) d) Emission spectra of **A** and **C** in methanol after nitrogen bubbling (concentration: 1×10^{-5} mol/L, excitation: 365 nm) e) Photograph of emission of **A**, **B** and **C** taking through a filter cutting light below 550 nm

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mainly of **3-unenc**. As these species can be mutually converted and have the same molecular weight, the minor component was assigned as **3-monoenc**, in which only one of the CDs is encapsulated, while the other remains unencapsulated.

Subsequently, the emission spectrum of **C** (**3-enc**) was examined in methanol. After 30 min of nitrogen bubbling, the sample exhibited a broad band in the 400–550 nm region with peaks at 411, 451, 512 nm, and an intense peak at 573 nm. In contrast, before nitrogen bubbling, only a broad band in the 400–550 nm region was observed and the 573 nm peak was absent (Fig. 2c). The emission of the benzil molecule was attributed to fluorescence at 430 and 505 nm at room temperature and to phosphorescence at 523 nm at 77 K by Bhattacharya et al.[20] Therefore, the 573 nm emission can be assigned to phosphorescence, namely RTP. In contrast, the emission spectrum of **A** obtained under the same conditions showed no phosphorescence peak (Fig. 2d). These results indicate that encapsulation is essential for benzil phosphorescence. The phosphorescence intensities of **A**, **B,** and **C** were also measured in methanol after nitrogen bubbling for 30 min: **C** showed the highest intensity, while **A** showed the lowest (Fig. 2e). In summary, while **3-enc** was synthesized and shown to exhibit RTP, its solvent-dependent unencapsulation could not be suppressed, highlighting the limitations of this system.

To overcome this limitation, bulky end-capping moieties were introduced into **3-enc** and **3-unenc** via a click reaction with benzyl azide, affording **4-enc-cap** and **4-unenc-cap**, respectively (Fig. 3a). The emission properties of **4-enc-cap** and **4-unenc-cap** were examined in solvents at room temperature. In chloroform, the emission spectrum of **4-enc-cap** after nitrogen bubbling for 30 min displayed a peak at 573 nm (Fig. 3b), which disappeared upon subsequent oxygen bubbling, confirming its phosphorescent origin. In contrast, **4-unenc-cap** showed no corresponding peak under the same conditions (Fig. 3c). Furthermore, the emission spectra of **4-enc-cap** exhibited phosphorescence regardless of the solvent used. In these measurements, the fluorescence maxima red-shifted in polar solvents (Fig. S22), indicating positive solvatochromism arising from the structural relaxation of the excited singlet state.[14a] In contrast, the phosphorescence maximum wavelength was 575 nm in toluene, 574 nm in chloroform, 573 nm in acetonitrile and 575 nm in dimethyl sulfoxide, remaining nearly constant across solvents. This is likely because the triplet state is less sensitive to solvent polarization.[21] In addition, the phosphorescence quantum yield of **4-enc-cap** was 4.7% in toluene, 6.8% in chloroform, 5.1% in acetonitrile and 3.8% in dimethyl sulfoxide. In other words, **4-enc-cap** exhibited RTP in diverse solvents, including polar solvents, as the end-capping moieties permanently lock the encapsulated structure. In addition, **4-**

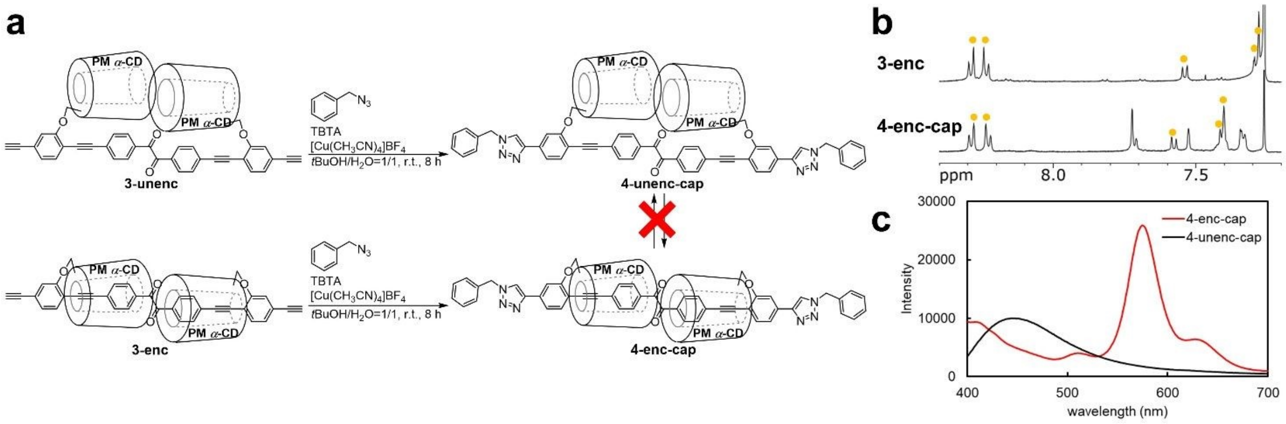

Figure 3. a) Synthetic procedure of **4-unenc-cap** and **4-enc-cap** b) ^{1}H NMR spectra of **4-enc-cap** and **3-enc** in $CDCl_3$ (aromatic region). c) Emission spectra of **4-enc-cap** and **4-unenc-cap** in chloroform after nitrogen bubbling (30 min). (concentration: 1×10^{-5} mol/L, excitation: 365 nm)

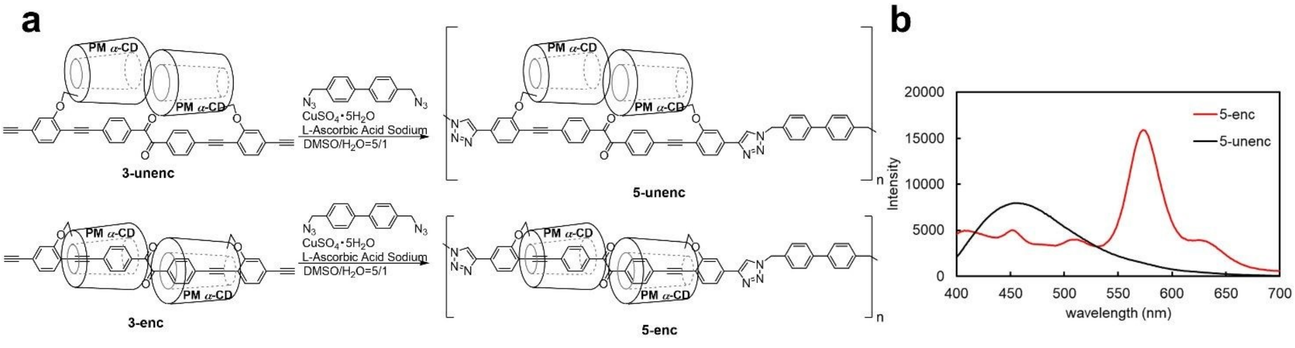

Figure 4. a) Synthetic procedure of **5-unenc** and **5-enc**. b) Emission spectra of **5-enc** and **5-unenc** in chloroform after nitrogen bubbling (30 min). (excitation: 365 nm)

enc-cap exhibited phosphorescence in the amorphous state with a yield of 2.8%. These results confirm that **4-enc-cap** retains RTP in both solvents and the amorphous state.

Using this encapsulated structure as a design motif, we synthesized a phosphorescent polymer with a high density of emissive units. Polymers are attractive as practical device materials because of their superior processability and thermodynamic stability compared with low-molecular-weight compounds. Conventional polymers, primarily conjugated, often suffer from strong π–π stacking interactions, which promote aggregation-caused quenching. In contrast, the steric bulk of the encapsulated units effectively suppressed interchain aggregation, allowing the benzil moieties to maintain their phosphorescent properties, even in the condensed phases. Based on this concept, we designed polymer **5-enc** as shown in Fig. 4a. The click polymerization between **3-enc**/**3-unenc** and 4,4’-bis(azidomethyl)biphenyl, which was synthesized according to the literature[22], yielded **5-enc**/**5-unenc**. The progress of polymerization was confirmed by size-exclusion chromatography (Fig. S23, S24). The phosphorescence properties of **5-enc** and **5-unenc** were examined in solution at room temperature. After nitrogen bubbling for 30 min, a phosphorescence peak at 573 nm was clearly observed only for **5-enc** (Fig. 4b), demonstrating that encapsulation was essential for RTP emission. The phosphorescence maximum wavelength of **5-enc** closely matched that of **4-enc-cap**, suggesting that both species have a comparable conjugation length. The phosphorescence quantum yield of **5-enc** was 4.0% in chloroform and 2.9% in the film state, confirming that efficientemission was retained, even in the condensed phase. These results indicate that encapsulation effectively suppresses nonradiative deactivation arising from π-π interactions, highlighting the potential of this polymer as a phosphorescent film, optical information storage material, or security ink.[10a-c]

In conclusion, we have demonstrated an effective strategy for achieving RTP from a benzil core in diverse solvents by using cyclodextrins for encapsulation and introducing capping moieties to lock the encapsulated structure. As a result, the encapsulated and capped benzil (**4-enc-cap**) exhibited phosphorescence in solvents regardless of their polarity. In addition, this molecule exhibited phosphorescence both in the amorphous state and as a polymer (**5-enc**). These results demonstrate that the present design concept is effective for realizing organic RTP in multiple physical states, including diverse solvents, and suggest that further molecular designs based on this approach will broaden the range of organic RTP materials.

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Conflicts of interest

There are no conflicts to declare.

Data availability

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The data supporting this article are included in the Supplementary Information (SI). Supplementary information is available. See DOI:

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Data availability

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