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# Photo-polymerization-induced tightened domain enhancing the room-temperature phosphorescence emission†

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Effectively enhancing the room-temperature phosphorescence (RTP) emission of pure organic phosphors is the goal that scholars continue to pursue. In this study, as a novel strategy, diacetylene monomers were introduced into a pure organic molecule, 2-(9H-carbazol-9-yl)ethanol (CZEO). Upon UV irradiation, the formed polydiacetylene (PDA) backbones caused a significant enhancement in the RTP emission. RTP emission continuously enhanced with the time UV irradiation. In addition, the synergistic enhancement with the help of halogen bonds was realized by introducing Br atoms into the CZEO unit.

## 1. Introduction

In recent years, scholars have made continuous attempts to enhance the room-temperature phosphorescence (RTP) efficiency of pure organic phosphors (POPs).<sup>1–5</sup> Compared with inorganic and organometallic counterparts, POPs have many advantageous properties such as large design windows, readily tunable properties, easy processability, and economic material cost.<sup>6,7</sup> However, developing POPs possessing highly efficient RTP is very challenging as both the rate of intersystem crossing (ISC) from the lowest excited singlet state ( $S_1$ ) to the triplet manifold ( $T_n$ ) and the rate of radiative deactivation from  $T_1$  to the ground state ( $S_0$ ) are very slow.<sup>8,9</sup> The rate of ISC can be greatly promoted following the El-Sayed rule in some organic molecules, such as aromatic carbonyls and nitrogen heterocycles through efficient spin-orbit coupling (SOC) by the effective mixing of the singlet and triplet states of different molecular orbital (MO) configurations.<sup>10,11</sup> Importing halogen atoms into organic molecules and/or reducing singlet-triplet splitting energy ( $\Delta E_{ST}$ ) are also effective strategies to improve the ISC rate.<sup>12,13</sup> However, even so, the SOC efficiency in POPs remains low compared to organometallic complexes. For the purpose of achieving a decent RTP efficiency in POPs, very

recently, Shao *et al.* demonstrated the design concept of “heavy atom-oriented orbital angular momentum manipulation” (HAAM) addressed a synergetic relationship in the promotion of SOC between heavy atoms and organic moieties exerting orbital angular momentum change. As a creative strategy, HAAM tailor-designed the intrinsic SOC efficiencies of POPs over  $10\text{ cm}^{-1}$  and a sub-ms phosphorescent lifetime.<sup>14</sup>

On the other hand, external nonradiative decays from  $T_1$  to  $S_0$  *via* ISC and quenching by the host matrix and oxygen at ambient conditions also severely affect the RTP efficiency of POPs. Therefore, suppression of collisional quenching as the major nonradiative decay route is another important approach to improve RTP efficiency.<sup>15,16</sup> For this purpose, common methods are to prepare POP crystals<sup>12,17</sup> and embed them into rigid amorphous matrices,<sup>18,19</sup> the cavity of cyclodextrin<sup>20,21</sup> or inorganic crystals,<sup>22,23</sup> leading to specific intermolecular forces between POPs and the surrounding environment. Herein, a simple and well-known pure organic molecule carbazole (CZEO) moiety was combined with diacetylene (DA) monomer (10, 12-pentacosadiynoic acid, PCDA) to prepare a novel POP polymeric system that demonstrates continuously enhanced RTP emission upon UV irradiation. It is known that when well-ordered DA monomers are irradiated by UV light, blue-phase polydiacetylene (PDA) is formed with its main absorption at  $\sim 640\text{ nm}$ .<sup>24–26</sup> The enhanced RTP emission of CZEO-PCDA assemblies is considered to be the extensively conjugated enyne backbones of PDA, which further suppressed the collisional quenching of the CZEO units. In addition, to confer halogen bonds, single and double Br atoms were imported into CZEO units, as shown in Fig. 1. Compared to the initial ones, upon UV irradiation, the RTP emission of CZEO-PCDA, Br-CZEO-PCDA and Br<sub>2</sub>-CZEO-PCDA assemblies were enhanced by 3.21, 3.54

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