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ARTICLE

Cyclic Boron Esterification: Screening Organic Room Temperature Phosphorescence and Mechanoluminescence Materials

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Aryl boronic acids are a broad class of organic intermediates. Here, we present that their cycle-esterification with proper dihydric alcohols is a simple and effective approach to screening organic room-temperature phosphorescence (RTP) and mechanoluminescence (ML) materials. Non RTP and ML active 4-(carbazol-9-yl)phenylboronic acid can be made to long-lived RTP emitters with the lifetimes of 264 and 430 ms and bright ML dye with blue emission by cycle-esterification with 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and glycol, respectively. Systematical single crystal analyses and quantum chemical calculations indicate that cyclic borates can dominate the molecular packing structures and the intermolecular interactions, which is responsible for their different optical properties.

Introduction

The material world was full of magic optical phenomena, and conjugated molecules have become promising light-emitting materials. For example, upon electro-, photo- and mechanical-excitation, some of them could produce electroluminescence (EL), photoluminescence (PL), and mechanoluminescence (ML), etc.[1–3] Recently, pure organic luminophors with room-temperature photophosphorescence (RTP) and ML properties have become attractive alternatives because they have the advantages of low cost, structure flexibility, appreciable stability, and good processability in comparison with those expensive, toxic and environmentally unfriendly metal-containing inorganics and organics.[4] The renewed and extensive attention on organic RTP materials was due to their potential applications in optics, electronics, and biology area,[5] and the increasing interest in ML materials was ascribed to the recognition of their potential applications in display, lighting, bio-imaging, and stress sensing as well as their academic significance in understanding the photophysical process.[6] However, up to now, only limited pure organic long-lived RTP[5,7] and bright ML[3e-3i,8] materials were reported, and it is hard or even impossible to predict in advance whether a newly prepared luminophor could display desirable optical properties. For example, the fresh 9-*H*-carbazole could emit commendable RTP and naked-eye-visible weak ML in the dark, but only limited carbazole derivatives could be made to exhibit impressive RTP and ML.[3g,5,7b-7f,8a,9] Also, some aryl boronic acids were reported to be RTP emitters,[5e] however, we found that 4-(carbazol-9-yl)-phenylboric acid (NPC-BA) was neither RTP nor ML active, despite it could be regarded as the derivative of RTP root carbazole and bright ML *N*-phenylcarbazole (NPC) (Chart 1).[3g,9b] On the other hand, both 3,5-diphenylphenylboric acid and *m*-terpyridylphenylboric acid were non-ML active, but their cyclic boron esters with pinacol emitted bright ML.[3h,3i] This intrigued us to esterify NPC-BA with pinacol (Chart 1). However, the obtained TME was still neither ML nor RTP active. These results further signified the complexity of structure–property relationship and also stimulated us to further cycle-esterify NPC-BA with other dihydric alcohols.

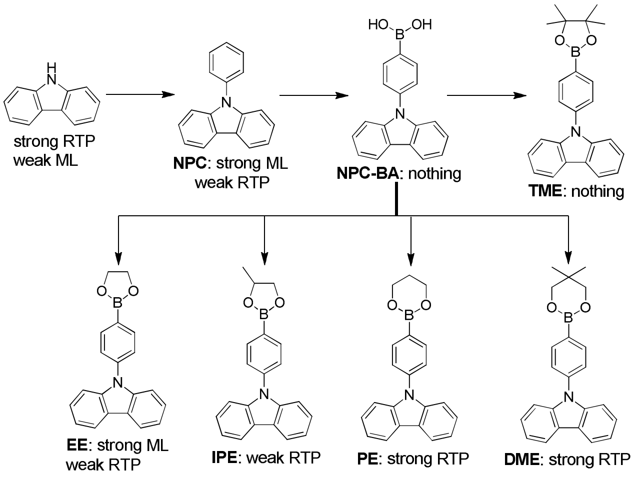

Chart 1. Structures and synthetic route of new carbazole-based cyclic boron esters and their RTP and ML function preview.

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†Electronic Supplementary Information (ESI) available: Details for synthesis and characterization Figure S1–Figure S11, Table S1–S2, crystallographic data and CCDC code and others. See DOI: 10.1039/x0xx00000x

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Results and discussion

The cyclic boron esters could be readily synthesized by the simple reaction of commercially available NPC-BA with various cheap dihydric alcohols and purified by a silica gel column chromatography in high yields. They were characterized by NMR, MS spectra and element analysis, and the obtained crystalline powders showed the melting points ranging from 150 to 208 ^{o}C (Figures S1–4, see the Supporting Information). NPC-BA emitted the near ultraviolet (NUV) light in THF solution, and all the cyclic boron esters exhibited the same absorption and the similar emission spectra in ultraviolet (UV) regions owing to the esterification-reduced solvatochromic effect (Figure S5). Moreover, in the room-temperature crystalline states, all the cyclic boron esters also exhibited same fluorescence spectra in UV regions, and NPC-BA crystal emitted a broad NUV light (Figure S5). These results indicated that cyclic boron esters hardly affected the solution and solid fluorescence properties. However, these cyclic boron esters and NPC-BA emitted the long-lived blue phosphorescence with

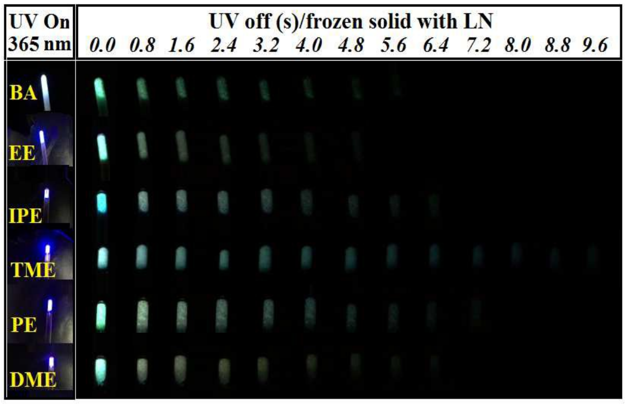
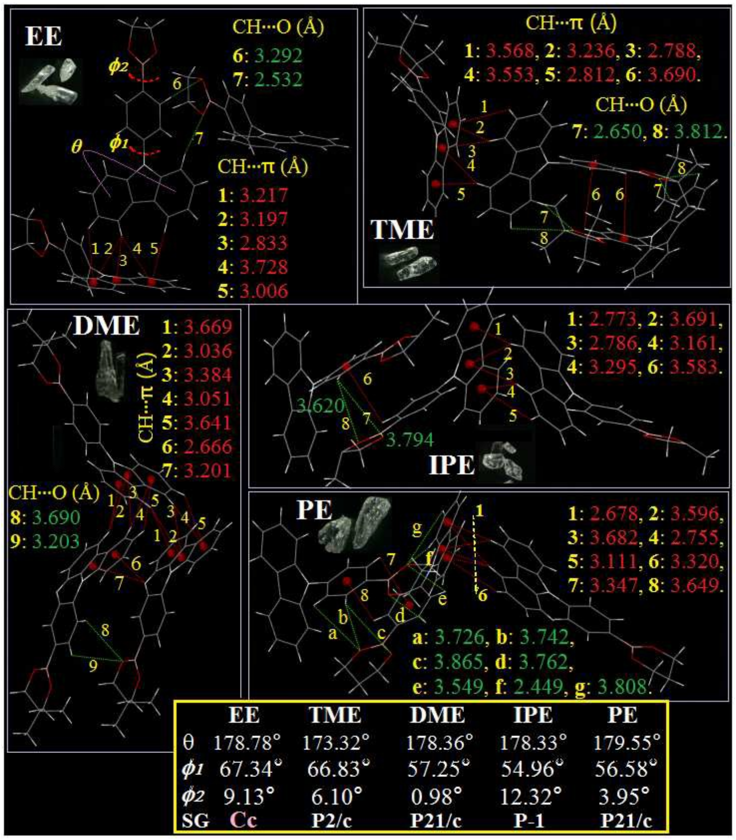


Figure 1. The photoluminescence photos of the frozen crystalline powders in liquid nitrogen upon UV on and after UV off.



	EE	TME	DME	IPE	PE
θ	178.78°	173.32°	178.36°	178.33°	179.55°
ϕ_1	67.34°	66.83°	57.25°	54.96°	56.58°
ϕ_2	9.13°	6.10°	0.98°	12.32°	3.95°
SG	Cc	P2/c	P21/c	P-1	P21/c

Figure 2. The intermolecular interactions among the adjacent three molecules in single crystals. The dihedral angles between two phenyl ring of carbazole (θ), between phenyl and carbazole (ϕ_1), and between phenyl and cyclic boron ester (ϕ_2) as well as the crystal space groups were summarized in the bottom table.

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the lasting times of 15–20 seconds in the frozen THF solution (Figure S6).

In the frozen crystalline states, all the cyclic boron esters and NPC-BA emitted green phosphorescence with the naked-eye visible lasting times of 6–10 s (Figure 1). The long-lived afterglow in both frozen solution and solid states indicated that these carbazole derivatives were all inherent phosphors. Generally, the triplet excitons for phosphorescence emission in organic luminophors came from the inter-system crossing (ISC) of the lowest singlet ones, and the heteroatoms (like N), the strong intermolecular interactions, and the spatially separated frontier molecular orbitals were favorable to ISC process. Thus, we first analyzed the crystal structure. Fortunately, excepting NPC-BA, all the cyclic boron esters could grow up good quality single crystals suitable for X-ray crystallographic analysis.

Single crystal analyses indicated that all the cyclic boron esters adopted the highly twisted molecular conformations to pack each other without strong π–π interactions (Figure 2 and Figure S7). The dihedral angles between phenyl and carbazole (ϕ_1), between phenyl and cyclic boron ester (ϕ_2), and between two phenyl rings of carbazole (θ) were all different. EE and TME exhibited large both ϕ_1 and ϕ_2, and TME and IPE had the most bent θ (173.32^o) and the largest ϕ_2 (12.32^o), respectively. It was noted that the very small ϕ_2 was observed for DME and PE with six-membered boron ester ring. The inspection on intermolecular interactions revealed that there were strong and multiple CH⋯π and CH⋯O interactions among molecules, and the typical interactions among the adjacent three molecules were depicted in Figure 2. On the whole, the intermolecular interactions in DME (twelve CH⋯π and two CH⋯O) and PE (eight CH⋯π and seven CH⋯O) crystals were relatively stronger, which could usually impede the molecular thermal motion and nonradiative transition of triplet excitons to contribute much to RTP.

Figure 3 indicated that these cyclic boron ester powders exhibited very different RTP lasting times in ambient air. No naked-eye visible RTP was observed for TME after UV off, and EE and IPE also showed weak RTP, although they all exhibited the commendable low-temperature phosphorescence and the RTP spectra (Figure 1 and Figure S8). Time-resolved PL-decay curves revealed that their RTP life-times were only 0.01, 7.2, and 0.21 ms, respectively (Figure S9). In sharp contrast, PE and DME powders exhibited impressive long-lived RTP with the lifetimes up to 264 and 430 ms, respectively. It seemed that the bent carbazole ring and large ϕ_1 and ϕ_2 were unfavorable to RTP. On the other hand, we thought that the big RTP difference for these cyclic boron ester powders was probably caused mainly by their different thermal and oxygen sensitivity, which was rather complex and rarely mentioned at present.

To further understand the phosphorescence behaviors, the time dependent-density function theory (TD-DFT) calculations based on the three strong interacted molecules derived from the single crystal structure were carried out by the Gaussian 09 program. The exciton energies of the n-th singlet (S_n) and n-th triplet states (T_n) were obtained on the corresponding ground state structure using the TD-B3LYP/6-31G*. Considering that the same transition orbital compositions with the energy level difference within ± 0.3 eV between T_n and S_1 were the more possible ISC channels, the calculated results indicated TME, EE and IPE could all contribute promising ISC channels in terms of their large integrated transition probability and exothermal energy gap (Figure 4 and Table S1), and the possible ISC channels for DME, PE and NPC-BA were relatively low probabilistic and endothermal. Moreover, a large overlap between HOMO and LUMO was displayed in NPC-BA, which was unfavorable to process for donor–acceptor type molecules and weakened the phosphorescence of NPC-BA.[10] For these cyclic boron esters, the highly twisted conformations were conducive to lowering electronic coupling and dissociating frontier orbitals. Overall, these calculation results could support the impressive low-temperature phosphorescence but not the different RTP. This further emphasized that, in most cases, it could be deficient to evaluate RTP by the intermolecular interactions and quantum calculation results since the RTP might be the residual inherent (low temperature) phosphorescence after thermal-inactivation and oxygen-quenching. Nevertheless, the cyclic boron esteri-fication was an effective approach to screening RTP emitters.

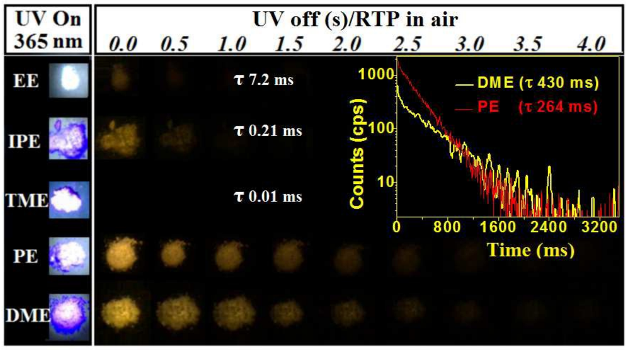

Figure 3. The room temperature photoluminescence photos of the crystalline powders upon UV on and after UV off in the dark. The inset was the corresponding RTP decay curves, and the RTP lifetimes (τ) were marked.

Inspired by that both esterified 3,5-diphenylphenylboric acid and *m*-terpyridylphenylboric acid with pinacol as well as *N*-phenylcarbazole (NPC) were high ML active, we esterified 4-(carbazol-9-yl)phenylboric acid with pinacol but found that

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TME was non ML active. Inspection on the crystal structure indicated that TME is not a piezoelectric space group (P2/c, the interpolation table in Figure 2),[3d,11] which was responsible for its non ML activity because of the strong correlation between ML event and piezoelectric effect.[8a,11] Further analyzing the crystal structures of other cycle boron esters revealed that only the EE crystal belonged to the piezoelectric space group (Cc, Figure 5a). This intrigued us to wonder that the crystalline EE powder was ML active or not. We ground the EE crystal and found bright blue emission in the dark (Figure 5b). Since the PL and ML colors looked like different, the ML spectrum was measured by a CCD spectrometer. The well matched ML and photofluorescence (PF) spectra were observed (Figure 5b), and no naked-eye-visible and CCD spectrometer-detectable mechanophosphorescence (MPP) was found. Thus, the ML and PF were from the same excited state (S_1), regardless of the modes of excitation. The lack of MPP was possibly due to either the weak phosphorescence or the different ISC transitions upon mechanical action, which was still unclear at present. Overall, the ML property was ascribed to the nature of piezoelectric space group, and the bright ML was related to

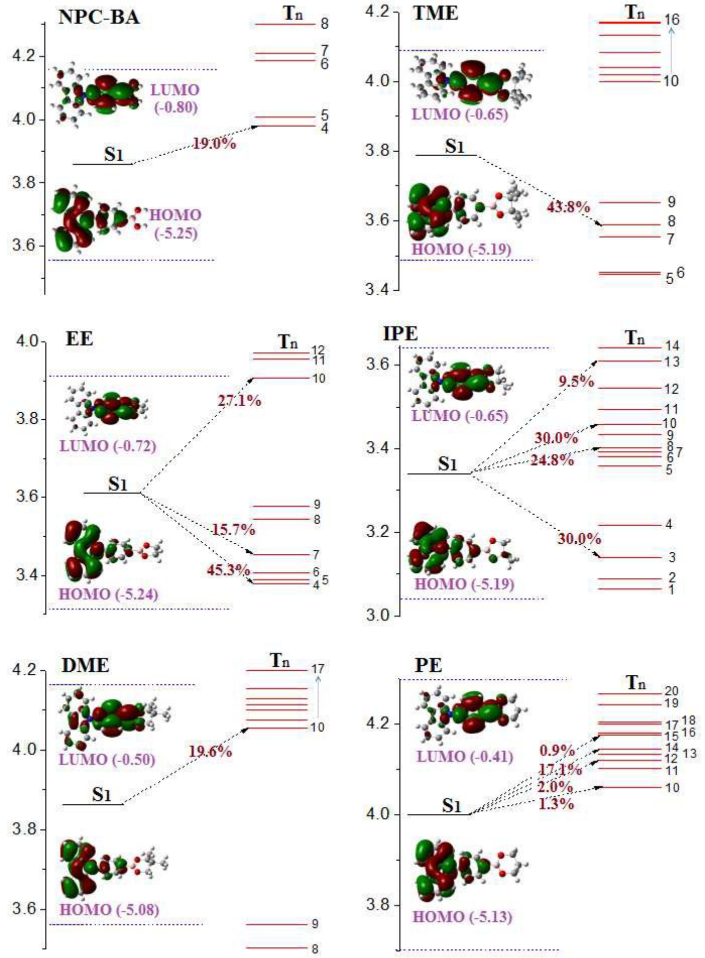

Figure 4. Energy level diagrams and possible ISC channels from singlet S_1 to triplet T_n (S_0 = 0 eV) based the adjacent three interacted molecules in the single crystal, where the percentage represented the integrated transition probability (%) under the same transition orbital composition. The insets were the frontier molecular orbital plots. (Gaussian 09, TD-B3LYP/6-31G*).

Table 1. Phosphorescence and luminescence of e properties of EE, TME, DME, IPE and PE at 298 K.

Name	EE	TME	DME	IPE	PE
PL_{max} (nm)	$374^{a)}/366^{b)}$	$363^{a)}/366^{b)}$	$363^{a)}/370^{b)}$	$364^{a)}/367^{b)}$	$348^{a)}/368^{b)}$
$<\tau>_{PL.}$(ns)	$6.65^{a)}/8.65^{b)}$	$6.81^{a)}/8.11^{b)}$	$8.75^{a)}/8.44^{b)}$	$7.88^{a)}/8.91^{b)}$	$6.74^{a)}/9.69^{b)}$
Φ_{PL}	$0.26^{a)}/0.33^{b)}$	$0.22^{a)}/0.44^{b)}$	$0.39^{a)}/0.38^{b)}$	$0.43^{a)}/0.37^{b)}$	$0.47^{a)}/0.42^{b)}$
Phos. $_{max}$ (nm)	$553^{b)}$	$525^{b)}$	$545^{b)}$	$550^{b)}$	$553^{b)}$
$<\tau>_{Phos.}$(ms)	$0.21^{b)}$	$0.01^{b)}$	$430^{b)}$	$7.2^{b)}$	$264^{b)}$
ML $_{max}$ (nm)	$372^{b)}$	—	—	—	—

a) Compounds in THF solution, the solution concentration was 1.0 × 10^{-5} M.; b) crystal powder.

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strong intermolecular interactions that should greatly reduce the possible energy loss through nonradiative relaxation and enhance the energy release upon crystal fracture. Finally, the small molecular size and regular structure could render EE with the moderate melting point (208 °C) and easy-crystallization, together with the bright UV emission (372 nm), EE could serve as a ML matrix to prepare full color ML materials at will by doping various color fluorophores, which was underway in our laboratory.

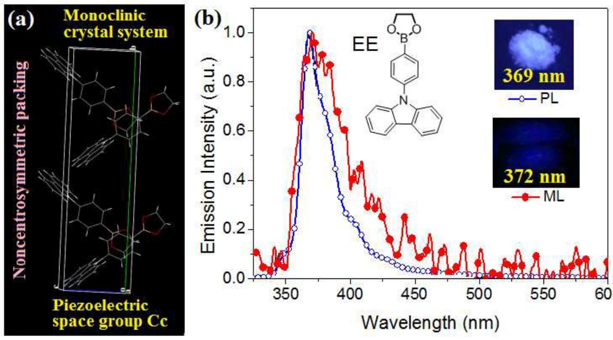

Figure 5. (a) The unit cell of EE crystal and (b) the photofluorescence (PL) and mechano-luminescence (ML) photos and spectra of crystalline EE powder.

Conclusions

In summary, we have demonstrated that cycle esterification of arylboronic acids with proper dihydric alcohols is a simple and effective approach to screening RTP and ML materials. The cyclic boron esters can dominate the molecular packing modes and the intermolecular interactions. However, evaluating RTP of organic crystals directly by intermolecular packing and inter-actions as well as quantum calculation results might be deficient because of the existence of complicated thermal-inactivation and oxygen-quenching on RTP. In contrast, organic crystals with piezoelectric space group and strong inter-molecular interactions can usually contribute much to high ML activity. Since arylboronic acids are a broad class of easily available organic intermediates, their cycle boron esters should become a treasure house of finding promising RTP and ML materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Cycle esterifying arylboronic acids with diols is a promising avenue to screen organic room temperature phosphorescence and mechanoluminescence materials.