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ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



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Persistent room temperature phosphorescence (*p*-RTP) of pure organic compounds is drawing much attention for its unique advantages and promising applications in anticonterfeiting, encryption, bioimaging, etc. Achieving efficient *p*-RTP, however, remains challenging. In this contribution, we designed and synthesized three benzoic acid-carbazole conjugates, 4-BACZ, 3-BACZ and 2-BACZ, with strong hydrogen bonding and dimer sturcture in their crystals. Comapred with their ester counterparts, whose highest RTP efficiency (Φ_p) is 2.6%, these acids exhibit significantly boosted Φ_p of 6.9%, 3.4% and 2.6% for 4-BACZ, 3-BACZ and 2-BACZ and 2-BACZ, respectively. Such enhancement should be ascribed to the effective and aboundant hygrogen bonding in the crystals, which significantly depressed the vibrational dissipations. This effect is also confirmed by the theoretically calculated much lower reorganization energies. These crystals are also readily fabricated into biocompatible nanoparticles (NPs) with inherited *p*-RTP characteristic. Such *p*-RTP feature of the crystals and NPs endows them highly promissing for versatile applications. Herein, anticounterfeiting and high resolution in vivo afterglow bioimaging adopting these materials are demonstrated.

Introduction

Published on 02 July 2019. Downloaded on 7/3/2019 12:01:15 AM

Pure organic compounds with persistent room temperature phosphorescence (p-RTP)¹⁻¹⁹ are drawing much attention for their unique advantages, such as long emission lifetime, low cost, easy processability,²⁰⁻²⁵ and promising applications in bioimaging, sensing, encryption, anticounterfeiting, etc.^{9,10,17,26-30} Moreover, apart from conventional conjugated molecules, p-RTP is also observed from nonconventional luminogens.^{10,31-33} However, compared with inorganic and metal-containing phosphors,³⁴⁻³⁶ pure organic RTP is difficult to accomplish, on account of their forbidden nature and the susceptibility of triplet excitons.³⁷⁻⁴¹ Meanwhile, p-RTP quantum yields of pure

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- Electronic Supplementary Information (ESI) available: Detailed synthesis and characterizations; ¹H and ¹³C NMR spectral details; mass spectrometry details; single crystal structure details; video details; CCDC 1915584–1915586. For ESI and crystallographic data in CIF or other electronic format see. See DOI: 10.1039/x0xx0000x

organic compounds are quite low and generally below 5%.⁴² Such situation is caused by the weak spin-orbital coupling (SOC) and the difficulty to efficiently imped quenching and nonradiative deactivations.^{19-24,43,44} To reduce spin inhibition, heavy atoms, heteroatoms and aromatic carbonyls are often incorporated to promote the SOC.^{19-24,45-48} To depress nonradiative dissipations and quenching, relative rigid environments with good oxygen barrier properties are provided with methods like crystallization,^{20,37,38,49-51} host-guest doping,^{3,19,52} polymer matrix embedding^{39,53-55} and the formation of metal-organic framework (MOF).^{17,56} Although great progress has been made in recent years, it remains challenging for improving the *p*-RTP efficiency of pure organics.



Chart 1. Structures of 4-BACZ, 3-BACZ, 2-BACZ and their corresponding esters and the schematic illustration of the dimers in the crystals. PL efficiencies of the crystals (Φ_c) and their *p*-RTP efficiencies (Φ_p) are also given. The photophysical data of the esters were adopted from ref [57].

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Very recently, we reported the p-RTP emission of methyl 4-(9Hcarbazol-9-yl)benzoate (4-MBACZ), methyl 3-(9H-carbazol-9yl)benzoate (3-MBACZ) and methyl 2-(9H-carbazol-9-yl)benzoate (2-MBACZ) (Chart 1) from their both crystalline and amorphous states.⁵⁷ Despite owning moderate photoluminescence (PL) efficiencies (6.5~37.6%), their *p*-RTP efficiencies (Φ_p) are low (\leq 2.6%). Further improving the $arPsi_{
m p}$ values is of crucial importance to their real-world applications, which could be realized through rational molecular and crystal engineering.²⁰⁻²³ In this contribution, to obtain more efficient p-RTP luminogens, we converted the ester groups of MBACZ into carboxyl units. The elimination of the relatively bulky methyl group is helpful to generate much denser molecular packing in crystals. Furthermore, the presence of carboxyl moiety is expected to generate effective hydrogen bonding, which is beneficial to boost both efficiency and lifetime of p-RTP owing to the stabilization of triplet excitons. Indeed, all three isomers, 4-(9H-carbazol-9yl)benzoic acid (4-BACZ), 3-(9H-carbazol-9-yl)benzoic acid (3-BACZ) and 2-(9H-carbazol-9-yl)benzoic acid (2-BACZ) exhibit hydrogen bonded dimer structure with $arPsi_{
m p}$ of up to 6.9%, which are remarkably boosted when compared with those of their esters (Chart 1). Their photophysical properties were thoroughly investigated and the isomeric effect is discussed. Notably, water dispersible nanoparticles (NPs) prepared from these acids also exhibit p-RTP emission, which were used for the in vivo afterglow bioimaging with high signal-tobackground ratio (SBR) of up to 62 being acquired.

Results and discussion

DOI: 10.1039/C9TC02879J The target compounds were easily obtained by the hydrolysis and consequent acidization of corresponding esters (Scheme S1, ESI⁺). They were fully characterized by ¹H and ¹³C NMR, high resolution mass spectrometry (HRMS) (Fig. S1-S9, ESI⁺) and Xray single crystal diffraction analysis (Table S1, ESI⁺), with satisfactory results being obtained.

In dilute tetrahydrofuran (THF) solutions (10⁻⁵ M), the absorption maxima of three compounds are mainly located at 293, 325 and 335 nm (Fig. S10, ESI⁺), which are similar to the corresponding esters.⁵⁷ We deduced that the 293 nm peak belongs to π - π ^{*} transitions, and the longer wavelength bands with well resolved structures should also be ascribed to the π - π^* transitions with hybrid local excited (LE) and charge transfer (CT) states.57 They emit bright blue light in THF, with PL maxima/efficiencies of 400 nm/87.7%, 405 nm/29.0% and 422 nm/20.2% for 4-BACZ, 3-BACZ and 2-BACZ (Table 1, Fig. S10, ESI⁺), respectively. When dopped in polymethyl methacrylate (PMMA) films with 1 wt% fraction, their emission maxima (E_m) are at 394, 399 and 407 nm for 4-BACZ, 3-BACZ and 2-BACZ, respectively (Fig. S11, ESI⁺), which are close to those of the corresponding solutions (Table 1). Their lifetimes are 6.5, 12.3 and 7.9 ns, respectively (Table 1, Fig S11, ESI⁺), and no noticeable signals could be acquired for the films with a delay time (t_d) of 0.1 ms, thus confirming their fluorescent nature.

Their solid emission was further studied. As shown in Fig. 1 and S12 (ESI⁺), the crystalline solids (Fig. S13, Video S1, ESI⁺) of three compounds exhibit blueish-white emission under 365 nm UV light. After ceasing the irradiation, orange or yellowish-



Fig. 1 (A) Photographs taken under 365 nm UV light or after ceasing the irradiation, (B) emission spectra and (C) *p*-RTP lifetimes of the crystals for 4-BACZ, 3-BACZ and 2-BACZ. (D) Comparison of the Φ_p values of 4-BACZ, 2-BACZ and their corresponding esters.

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orange lights lasting for several seconds are observed, which are corresponded to their p-RTP. 4-BACZ exhibits a prompt E_m at 429 nm. With a t_d of 0.1 ms, other than the original one, emerging E_m occurs at 549 nm together with a shoulder at ~594 nm (Fig. 1B). These results indicate that the emission at 429 nm comprises of both prompt and delayed fluorescence (PF and DF), whereas the others should be ascribed to the p-RTP emission, whose lifetime (< z>p) is 558 ms (at 549 nm) as determined by the time-resolved emission measurement (Fig. 1C).

Table 1 Photophysical properties of 4-BACZ, 3-BACZ and 2-BACZ.

	solution		film		crystal			
Sample	$\lambda_{f}{}^a$	<{\cbc}>_{f}^{b}	λ_{f}^{a}	<t>f^b</t>	$\lambda_{\mathrm{f}}{}^{a}$	λ_p^{c} (nm)	<{{{\it t}>_{{\rm f}}}^b}	<t>p</t>
	(nm)	(ns)	(nm)	(ns)	(nm)		(ns)	(ms)
4-BACZ	400	8.0	393	6.5	429	549/594	4.3	558
3-BACZ	405	5.0	398	12.3	441/484	546/592	13.8	602
2-BACZ	422	4.3	406	7.9	444/485	558/599	12.3	568

^a fluorescence peak(s). ^b fluorescence lifetime. ^c RTP peaks.

Similar to 4-BACZ, 3-BACZ and 2-BACZ emit simultaneous PF, DF and *p*-RTP. Their prompt emission spectra show the $E_{\rm m}$ s at 441/484 and 444/485 nm for 3-BACZ and 2-BACZ, respectively. With a t_d of 0.1 ms, other than above E_m s, new ones at 546/592 and 558/599 nm associated to the *p*-RTP emissions are noticed (Fig. 1B). The $\langle \tau \rangle_p$ values for 3-BACZ and 2-BACZ crystals were also determined, which are 602 (at 546 nm) and 568 ms (at 545 nm) (Fig. 1C), respectively. Notably, compared with their corresponding esters, the fluorescence of the crystalline acids are obviously bathochromically shifted from 402, 403 and 428 nm⁴⁹ to 429, 442 and 444 nm for 4-BACZ, 3-BACZ and 2-BACZ, accompanying lifetimes of 4.3, 13.8 and 12.3 ns (Fig. S13, ESI⁺), respectively. Such bathochromic shift might be ascribed to the dimer formation through hydrogen bonding (vide infra), which extends the effective conjugation length of the compounds. Their phosphorescence, however, depicts neglectable changes. To quantitatively evaluate the emission of the crystals, their quantum efficiencies (Φ_c) were measured, which are 53.3%,

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2.6%, which are significantly enhanced by 2.7, 4.9 and 26,0 fold with comparison to the esters (Fig. 1D). DOI: 10.1039/C9TC02879J

To gain more insights into their photophysical properties, single crystals of three acids were cultured and their structures were determined (Figs. 2, 3, Figs. S15, S16, Table S2, ESI⁺). As can be seen from Figs. S15 and S16 (ESI+), abundant and effective intermolecular interactions are present in all crystals. Taken 2-BACZ for example, O-H…O=C (1.835, 1.831 Å) hydrogen bonds, C–H…π (2.898, 2.760, 2.786, 2.835, 2.830 Å), C=O···O–H (2.651, 2.633 Å), O=C···H–O (2.729, 2.662 Å), O-H…H-O (2.304 Å), C-H…O=C (2.691 Å) short contacts and even $\pi \cdots \pi$ (3.321 Å) interactions are found in the crystals (Fig. S16, ESI⁺). These strong intermolecular interactions greatly imped the molecular motions to offer rigidified conformations;



Fig. 3 Fragmental molecular packing and exampled hydrogen bonds, $\pi {\cdots} \pi$ interactions, and short contacts among oxygen atoms of (A) 3-BACZ and (B, C) 2-BACZ crystals.



Fig. 2 Fragmental molecular packing and exampled hydrogen bonds, π ··· π interactions, and short contacts among oxygen atoms of 4-BACZ crystals.

17.4% and 12.7% for 4-BACZ, 3-BACZ and 2-BACZ, respectively.

meanwhile, the crystalline lattices also prevent the molecules The RTP efficiencies ($\Phi_{\rm p}$) were calculated as 6.9%, 3.4% and from contacting with triplet quenchers (i.e. oxygen, moisture),

thus synergistically generating bright *p*-RTP emission. Notably, there are abundant hydrogen bonds in acid crystals, which are absent in their ester counterparts. Taken 2-BACZ crystals for example, while large amounts of hydrogen bonds are present in 2-BACZ crystals, no typical hydrogen bonds exist in 2-MBACZ crystals.⁵⁷ The effective hydrogen bonding and other intermolecular interactions provide rigid conformations for 2-BACZ molecules, thus generating enhanced RTP emission when compared to that of 2-MBACZ crystals.

Notably, different from the esters, all acids readily form dimers through hydrogen bonds (Figs. 2 and 3). In particularly, O…O through space electronic interactions (2.604~2.644 Å), which would extend the conjugation of the compounds. The formation of the dimers in the acid crystals well explains why they exhibit much redder fluorescence than their esters. Meanwhile, acids also own much smaller torsion angles, especially for 4-BACZ and 2-BACZ (Figs. S17 and S18, Tables S3-S6, ESI⁺). For 4-BACZ and 2-BACZ, the mean torsion angles between carbazole (CZ) and benzoic acid (BA) are 49.7° and 70.4°, whereas those for 4-MBACZ and 2-MBACZ are 52.0° and 71.5°. As for 3-BACZ, despite it possesses a much larger mean torsion angle between CZ and BA than in 3-MBACZ, it shows a much smaller mean torsion angle between carboxyl and the benzene ring (0.8°, 7.5° for 3-MBACZ). Much smaller torsions also offer better conjugation, which work together with the dimers to yield red-shifted emissions.

To further elucidate the greatly enhanced $\mathcal{O}_{\rm p}$ of the acids, we calculated the excited-state electronic structures for all acids and their esters with the time-dependent density functional

peaks between them. Likewise, owing to the highly approaching ΔE_{SOT1} values, neglectable shifts of RTP peaks among/office/acids and the esters are reasonable.

Table 2 Reorganization energy (λ) and ΔE_{SOT1} of 4-BACZ, 3-BACZ, 2-BACZ and 4-MBACZ crystals.

sample	4-BACZ	3-BACZ	2-BACZ	4-MBACZ
λ/eV	0.3740	0.3813	0.4010	0.4124
ΔE_{SOT1} /eV	2.40	2.34	2.46	2.45

Given the high quantum efficiency, long afterglow and distinct emission colours with UV light on and off, these acids embrace promising applications in security technologies and in vivo bioimaging. As depicted in Fig. 5A, under 365 nm UV light, a blue star made up of the crystals of 4-BACZ is observed, whose color turns into orange and holds for several seconds after the stop of irradiation. This process is reversible and can be repeated for many times. These results illustrate the application prospective of the acids in multichannel anti-counterfeiting.

It is favourable for compounds with efficient *p*-RTP to be used for in vivo afterglow imaging,^{9,26-28} which can exclude the nanosecond tissue autofluorescence, thus offering more reliable observation than traditional fluorescent agents. Owing to their bright *p*-RTP in crystals, three acids were fabricated into NPs through the top-down method by encapsulating the solids with the amphiphilic copolymer PEG-*b*-PPG-*b*-PEG (F127) under continuous sonication, as demonstrated in Fig. S19A (ESI⁺). This approach could take advantage of having nanoscale size and orderly molecular packing of RTP luminogens. The resulting NPs of 4-BACZ, 3-BACZ and 2-BACZ can be well dispersed in water



Fig. 4 Energy level diagrams of BACZ and 4-MBACZ calculated by the QM/MM model.

theory (TD-DFT) method at the level of B3LYP/6-31G(d), including the energy level diagrams (Fig. 4) and natural transition orbitals (NTOs) of the lowest triplet state (T₁) (Fig. S19, ESI⁺). It is shown that the reorganization energies (λ) of 4-BACZ, 3-BACZ and 2-BACZ are 0.3740, 0.3813 and 0.4010 eV, being increased in order, which are also much smaller than that of 4-MBACZ (0.4124 eV, Table 2). Principally, the smaller λ means the more restricted nonradiative decay rate of T₁, which explains the increase of the Φ_p from 2-BACZ, 3-BACZ to 4-BACZ, and from esters to acids (e.g., 0.4124 eV for 4-MBACZ and 0.4010 eV for 4-BACZ). In addition, the energy differences between S₀ and T₁ states (ΔE_{S0T1}) for 4-BACZ (2.40 eV) and 4-MBACZ (2.45 eV) are less different (Table 2),^[57] which determines the less shift of the RTP with similar hydrodynamic diameter of 98.7, 101.7 and 110.4 nm (Fig. 5B–D), respectively. All NPs are highly stable, whose sizes are unchanged when stored at 4 °C for more than 6 d (Fig. S20B, ESI⁺). These NPs also inherit the *p*-RTP feature from their bulky crystals, among which 4-BACZ NPs present the strongest *p*-RTP intensity, presumably associated to its highest Φ_p and relatively good crystallization ability (Fig. 5B-D, inset). Furthermore, outstanding photo-bleaching resistance and little roll-offs of RTP intensities could be observed after 8 cycles or 80 min UV irradiation (Fig. S20C and D, ESI⁺).

Before the in vivo experiment, biological toxicity of the NPs was evaluated. As demonstrated in Fig. 5E, small amounts of cells decay after 24 h are noticed with the presence of varying concentrations of NPs, which indicates their very low

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Fig. 5 (A) Demonstration of the anticounterfeiting application of 4-BACZ. Photographs were taken under 365 nm UV light (left) and after ceasing the UV irradiation (right). The particle size distribution and in vitro phosphorescence imaging (inner) for 4-BACZ (A), 3-BACZ (B), 2-BACZ (C) NPs; (D) Cell viability assay of HeLa cervical cancer cells after staining with different concentrations of 4-BACZ, 2-BACZ NPs; (E) In vivo phosphorescence imaging based on 4-BACZ, 2-BACZ NPs.

cytotoxicity. Then live animals test was conducted, with 4-BACZ, 3-BACZ and 2-BACZ NPs being subcutaneously injected into the live nude mice. The mice were then transported into IVIS instrument, exposed to the 365 nm hand-held UV lamp. Images were immediately taken after moving the lamp under bioluminescent mode. Since the removal of real time excitation, phosphorescence avoided the interference the of autofluorescence from the skin of mouse, allowing the observation of the unique and relatively clear p-RTP signals of the NPs in living mouse. Notably, despite no remarkable signals could be observed for the 3-BACZ NPs in vivo, presumably owing to their weaker intensity, 4-BACZ and 2-BACZ NPs show clear afterglow images with high SBR values of 62 and 33 (Fig. S21, ESI⁺), which are comparable to those of previously reported examples.⁵⁸ These results suggest the acid NPs with *p*-RTP can be utilized in biomedical imaging.

Conclusions

In summary, we have successfully developed a series of efficient pure organic *p*-RTP ($\langle \tau \rangle_p \rangle$ 0.55 s) phosphors based on carbazole and benzoic acid moieties. Acidification of the esters of 4-MBACZ, 3-MBACZ and 2-MBACZ into acids significantly enhanced their phosphorescence efficiencies, with Φ_p values changing from 2.6%, 0.7% and 0.1% to 6.9%, 3.4% and 2.6%, affording the amplification of up to 26-fold. Such remarkable enhancement should be ascribed to the highly rigidified conformation through hydrogen bonding, which also results in much lower reorganization energies in crystals, as indicated by the theoretical results. Such outstanding *p*-PRT performances make them applicable in multiple fields, such as anticounterfeiting and biomedical imaging. The acids NPs were facilely fabricated through the top-down method with inherited *p*-RTP emission from their crystals. And moreover, 4-BACZ and 2-BACZ NPs can be used for the in vivo afterglow imaging, with SBR of up to 62, thus allowing the high-resolution imaging free of the interference of autofluorescence. These results further suggest the promising prospects of molecular and crystal engineering toward high performance pure organic *p*-RTP luminogens for diverse applications.

Live subject statement

All animal studies were performed in compliance with the guidelines set by Tianjin Committee of Use and Care of Laboratory Animals, and in compliance with the National Standard of the Peoples' Republic of China called Laboratory animal-Guideline for ethical review of animal welfare (GB/T 35892-2018), and the overall project protocols were approved by the Animal Ethics Committee of Nankai University.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (51822303, 51473092 and 51622305). W.Z.Y. also thanks the support of the medicine-

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engineering cross project of Shanghai Jiao Tong University (YG2016MS21).

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View Article Online DOI: 10.1039/C9TC02879J

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Pure organics with *p*-RTP efficiency enhanced through hydrogen bonding could be prepared into nanoparticles for in *vivo* imaging.