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Organic Guest-Host System Produces Room-Temperature Phosphorescence at Part-Per-Billion Level

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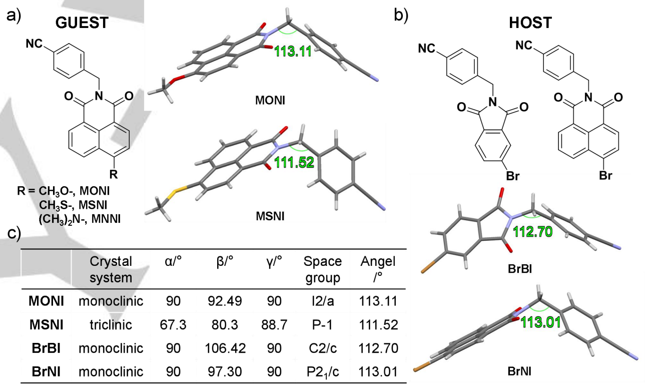
Abstract: Manipulation of long-lived triplet excitons in organic molecules are key to applications including next-generation optoelectronics, background-free bioimaging, information encryption and photodynamic therapy. However, organic room-temperature phosphorescence (RTP), which stems from triplet excitons, is still difficult to simultaneously achieve efficiency and lifetime enhancement on account of weak spin-orbit coupling and rapid nonradiative transitions, especially in the red and near infrared region. Here we report a series of fluorescent naphthalimides, which did not originally show observable phosphorescence in solutions, as aggregates, in polymer films, or in any other tested host materials including heavy-atom matrices at cryogenic temperatures, can now efficiently produce ultralong RTP (ϕ = 0.17, τ = 243 ms) in phthalimide hosts. Notably, red RTP (λ_{RTP} = 628 nm) is realized at a molar ratio of less than 10 parts per billion, demonstrating an unprecedentedly low guest-to-host ratio where efficient RTP can take place in molecular solids.

The modulation of long-lived triplet excitons is essential for a variety of processes such as photosynthesis,[1] solar cells,[2] OLED[3] and quantum computing.[4] Organic phosphors, being structurally flexible, spectroscopically tunable, stimuli-responsive and environmentally friendly, are outstanding candidates for the development of new generations of organic optoelectronic materials[5] and biomedical agents.[6] Consequently, extensive explorations have been initiated toward organic room-temperature phosphorescence (RTP) in the past few years,[7] and significant progresses have been accomplished in both theoretical and application prospects,[8] although organic phosphorescence is typically perceived as a feature at cryogenic temperatures or under air-free conditions.[9] However, organic RTP luminogens are not quite in juxtaposition to their inorganic counterparts in both phosphorescence efficiency and lifetime enhancement, which necessitates design strategies allowing for improved optical properties.[10] Herein, we report an organic guest-host system which converts strong guest fluorescence (**MONI**, **MSNI** and **MNNI** in Figure 1) into ultralong RTP via a tailored host (**BrBI**). It has to be noted that no guest RTP could be recorded in an exhaustive variety of solutions and matrices other than **BrBI** derivatives. Red RTP with an emission maximum *circa* 630 nm is realized. Distinct ultralong RTP is produced in the solid state by as few as <10 guest molecules for every 1 billion host molecules, i.e., <10 parts per billion (ppb), which is beyond the regular analytical methods (e.g., NMR,[11] HPLC[12] and HRMS[13]). The current study expands what the possible limit is, in order for the guest/host ratio to significantly alter the bulk optical properties in organic molecular systems.



	Crystal system	α/°	β/°	γ/°	Space group	Angel /°
MONI	monoclinic	90	92.49	90	I2/a	113.11
MSNI	triclinic	67.3	80.3	88.7	P-1	111.52
BrBI	monoclinic	90	106.42	90	C2/c	112.70
BrNI	monoclinic	90	97.30	90	$P2_1/c$	113.01

Figure 1. Stick models showing *sp*^{3}-carbon-linked organic donor-acceptor structures. a) Guest molecular structures and represent single-crystal X-ray diffraction (SC-XRD) structures **MONI** and **MSNI**. b) Host molecular structures and SC-XRD structures. c) Crystal lattice parameters.

Three *sp*^{3}-carbon-linked donor-acceptor naphthalimides, **MONI**, **MSNI** and **MNNI** (**MO** for CH_3O-, **MS** for CH_3S-, and **MN** for $(CH_3)_2N$-, Figure 1), as guest molecules and two host compounds (**BrBI** and **BrNI**), were facilely synthesized (Scheme S1) and characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra, high resolution mass spectrometry (HRMS), elemental analysis (EA) and high performance liquid chromatography (HPLC, Figure S1, Figure S17-S34). Crystal parameters (Figure 1c) obtained from single-crystal X-ray diffraction (SC-XRD) reveal that these molecules exhibit similar dihedral angles (111.52 ° -113.11 °) between the donor and acceptor planes, suggesting high structural similarity in the solid state. The absorption (solid lines) and emission spectra (dash lines) in dilute tetrahydrofuran (THF) are presented in Figure 2a: **MONI**, **MSNI** and **MNNI** exhibit intense (almost unity, Table S1) fluorescence while **BrBI** and **BrNI** have no discernible emission, likely due to the heavy-atom effect.[14] The absorption and emission onsets both indicate the energy level of the lowest electronic transition is gradually descending in the following order: **BrBI** > **BrNI** > **MONI** > **MSNI** > **MNNI** (Figure 2a and Table S1).[15]

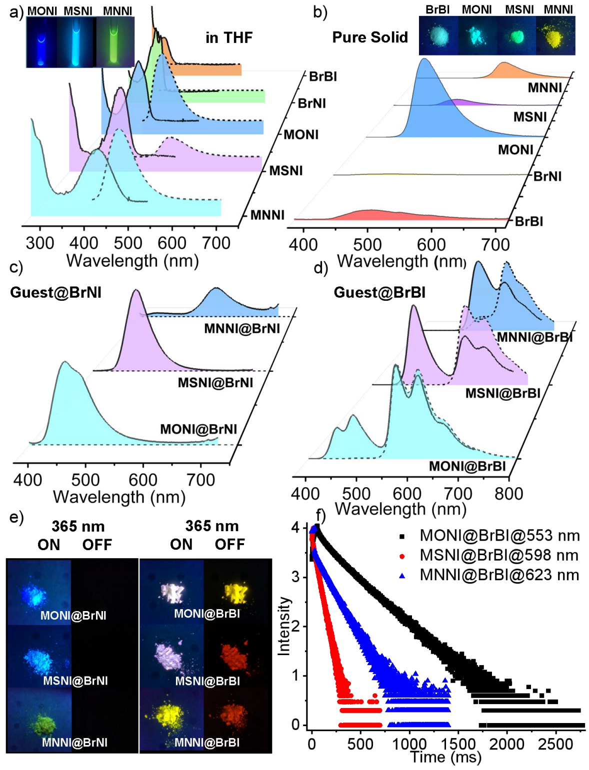


Figure 2. a) UV absorption spectra (solid lines) and photoluminescence (PL) spectra in THF (2x10^{-5} M) at 298 K (dash lines). Inset: photographs of **MONI**, **MSNI** and **MNNI** under 365-nm light irradiation. b) Steady-state PL spectra of molecular solids. Inset: photographs of **BrBI**, **MONI**, **MSNI** and **MNNI** solid under 365-nm light irradiation. c) Steady-state PL spectra (solid lines) and delayed emission (DE, Δt = 0.1 ms, dash lines) spectra of guests (w/w 1%) in the **BrNI** host solid at 298 K (λ_{ex} = 365 nm). d) Steady-state PL spectra (solid lines) and DE (dash lines) spectra of various guests (w/w 1%) in the **BrBI** solid at 298 K (λ_{ex} = 365 nm). e) Photographs of combinations of three guests in two hosts during and immediately after 365-nm light irradiation. f) Time-resolved emission decay curves of the three guests in solid **BrBI**.

The solid-state emissions (Figure 1b) are highly fluorescent and redshifted compared to those in solution, except that **BrBI** shows weak photoluminescence (QY <0.5%, Figure S4 and Table S2). Specifically, **MONI**, **MSNI** and **MNNI** are only fluorescent with no detectable RTP in either solutions or solid state of various conditions (Figure 2b and S5, Table S3) and reducing the temperature to 77 K only results in a barely measurable long-lived decay component for **MSNI**, suggesting the extremely low intrinsic phosphorescence yield among the three molecules.

Surprisingly, when **BrBI** was used as a host medium, visually striking RTP could be instantly turned on for all three guest molecules (Figure 2d). These RTP lifetimes range from circa 40 ms to 240 ms. For the guest-host combination **MNNI@BrBI**, red RTP (maximun at 623 nm) was realized with a quantum yield (QY) up to 8.3% and a lifetime of 131.8 ms (Figure 2e, 2f and S6, Table 1), given that red organic RTP was usually suppressed due to the energy-gap law.[16] We ascribe the observed RTP emissions in these guest-host systems to the lowest triplet excited state from the guest molecules, respectively. This is evidenced by the phosphorescence spectra measured in 1, 6-diiodohexane at cryogenic temperature (Figure S7 b-d). However, when the host molecule is replaced by **BrNI** (Figure 2c), no RTP could be observed or recorded. Both experiments suggest that external heavy-atom effect is not the dominating cause for the RTP "turn on".

Table 1. Photoluminescence properties of dopant samples at room temperature.

Samples[a]	F max (nm)[b]	Lifetime (ns)[c]	P max (nm)[d]	Lifetime (ms)[e]	QY$_P$ (%)[f]
MONI@BrBI	465	1.90	554	243.07	17.4
MONI@BrNI	470	1.62	/[g]	/	/
MSNI@BrBI	474	1.99	599	42.48	12.6
MSNI@BrNI	467	1.16	/	/	/
MNNI@BrBI	542	4.80	623	131.77	8.3
MNNI@BrNI	562	0.91	/	/	/

[a] Guest-host molecular solids (w/w 1%). [b] Fluorescence emission maxima of steady-state photoluminescence spectra excited at 365 nm. [c] Apparent fluorescence lifetime (naonoLED-370). [d] RTP maxima of delayed emission spectra excited at 365 nm. [e] Apparent RTP lifetime (spectraLED-370). [f] Absolute quantum yield from 450-750 nm at room temperature. [g] Too weak to measure.

We then studied the influence of guest/host ratio vs. RTP spectroscopic features, using **MSNI@BrBI** as an example. We found that for every 1 billion host molecules, a few (less than 10) guest molecules (i.e., 10 ppb, w/w) were sufficient for RTP "turn on", a limit unprecedented for binary organic RTP systems (Figure 3a and 3b). According to Figure 3b, the RTP intensity (λ_{RTP} = 598 nm) with a guest mass ratio of 10 ppb is *circa* 5 times higher than the baseline, which is delayed emission intensity obtained from pure **BrBI** solid at the same wavelength. As the number of guest molecules increases, the most intense RTP lies in a mass ratio range of 0.1% to 1.0% with the highest QY$_{RTP}$ = 15.1%. Delayed (Δt = 0.1 ms) excitation spectra (DEx) of **MSNI** guest (0%-15%) in the **BrBI** host medium (Figure S8) show that two new excitation peaks emerge (circa 362 nm and 423 nm), presumably due to the presence of the **MSNI** molecules (see red circle in Figure S8). More interestingly, when the DEx spectra were normalized at 362 nm (Figure S9a), the relative intensity at 423 nm band is enhanced with increasing guest content (Figure S9b) despite the same RTP energy and vibronic features, suggesting that various guest/host species contribute to the lowest **MSNI** T$_1$ state including aggregates in both the excited and ground states.[17] The PL spectra of **MSNI** guest (0%-15%) in **BrBI** host solid are presented in Figure 3c, where a 0.1% ratio leads to the highest absolute luminescence (F+RTP) QY = 35%. The fluorescence maximum (λ_F = 464 - 494 nm) blue-shifts first as a result of guest monomer fluorescence (λ_F = 463 nm) and then red-shifts due to guest aggregates fluorescence (λ_{FA} = 513 nm) beyond a guest mass ratio of 0.01% (Figure S10b). However, the highest RTP/F ratio is observed for a guest mass ratio of 10 ppm (Figure 3c and 3d), according to the steady-state emission spectra.

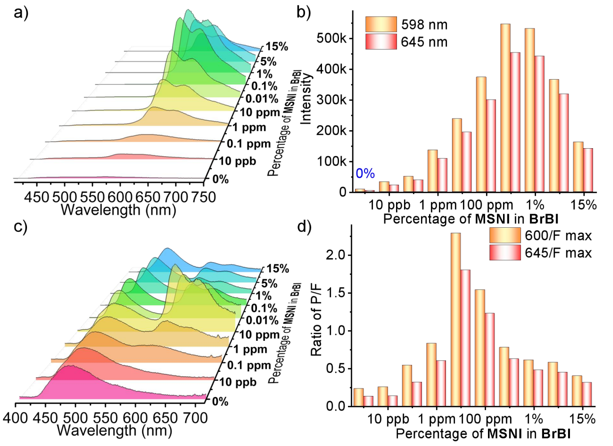


Figure 3. a) Delayed emission spectra of **MSNI** guests (w/w 0%-15%) in the **BrBI** solid at 298 K (λ_{ex} = 365 nm). b) Relative DE intensity at 598 nm and 645 nm vs. guest mass content. c) Normalized PL spectra of the **MSNI** guest (w/w 0%-15%) in the **BrBI** host solid in air at 298 K (λ_{ex} = 365 nm). d) Ratio of phosphorescence to fluorescence of the **MSNI**/**BrBI** solid as a function of the **MSNI** guest mass content.

To explore the mechanism behind of highly efficient RTP “turn on” from the binary guest-host system, we performed two groups of control experiments shown in Figure 4, respectively. In the first one, **BrBI** was replaced with **HBI**, a heavy-atom free version of the host molecule (Figure 4a). A second control (**DBrB** in Figure 4b) serves as a structurally similar but dibrominated (*sp*^{3}-linked twisted geometry) solid-state host for **MSNI**. The results show that the **HBI**, containing only C, H, O and N, produces strong RTP while **DBrB**, containing Br, fails to do so (Figure 4b, Table S4), indicating that the external heavy atom effect is not the main cause of binary RTP. Furthermore, we notice that more blue-shifted excitation (330 nm, where even higher energy excitation produces stronger RTP shown in Figure 4c, S11 and S12) is required in the **HBI** host in comparison to the **BrBI** host (365 nm), which match the solid-state absorption spectra of the two hosts (Figure S13). All evidence suggests efficient energy transfer occurs from host to guest molecules for the observed strong RTP,[18] the growing intensity of which is at the cost of the host excited states (Figure S14). This also explains the lack of appreciable luminescence emission in the **DBrB** host, which is most likely dominated by non-radiative decay processes so that it does not provide sufficiently long-lived triplet excitons to diffuse to the guest molecules.[19]

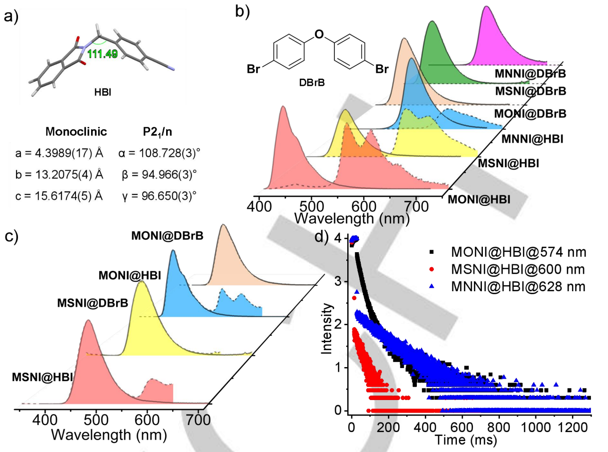


Figure 4. a) Chemical Structure of **HBI**. b) Steady-state PL spectra (solid lines, λ_{ex} = 365 nm) and delayed (Δt = 0.1 ms, λ_{ex} = 300 nm) emission spectra (dash lines) of various guests in **HBI** or **DBrB** (w/w 1%) host at 298 K. c) Steady-state PL spectra (w/w 1%) at 298 K with two different excitation wavelengths (λ_{ex} = 330 nm for dash lines, 365 nm for solid lines). d) RTP decay profiles of three guest molecules (w/w 1%) in **HBI**.

A simplified energy diagram is illustrated to propose the guest-to-host energy transfer process (Figure 5a): 1) the photon energy is first converted to triplet excitons of the host aggregates, which could be lower and longer than the monomeric host; 2) an efficient triplet-triplet energy transfer (TTET) between the delocalized host aggregates and guest molecules takes places;[20] 3) the guest molecule traps the triplet exciton and emits via the lowest triplet state (T_1). It has to be noted that for every guest, it is encircled by hundreds host molecules in a 3-dimensional cube. Such high efficiency can make the underlying mechanistic study extremely difficult and may require assistance from single-molecule techniques in the future. We also noted that with various guest/host ratios, different luminescence emission colors could be procured, exemplified in Figure 5b and 5c, including white-light emission useful in purely organic LED applications.[21]

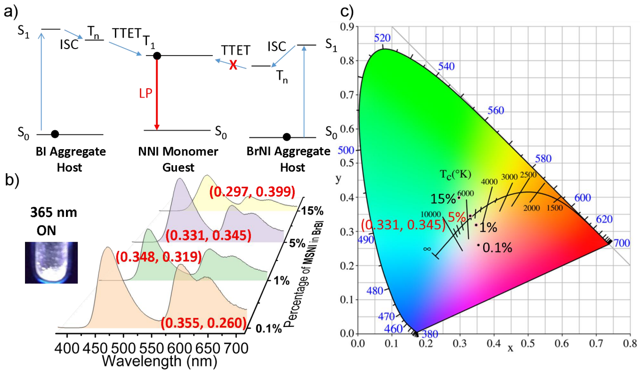


Figure 5. a) Proposed mechanism (ISC: intersystem crossing; TTET: triplet-triplet energy transfer; LP: long lifetime phosphorescence). b) Steady-state PL spectra of **MSNI** (w/w 0.1%-15%) in **BrBI** at 298 K (λ_{ex} = 365 nm). Inset: **MSNI@BrBI** (w/w 5%) under the 365-nm UV irradiation. c) CIE figure of **MSNI** (w/w 0.1%-15%) in the **BrBI** solid.

In summary, we have constructed a binary system turning nearly unity fluorescence into strong RTP with a quantum yield up to 17.4% and a lifetime up to 243 ms. A plausible mechanism was proposed based on experimental evidence, strongly pointing to the fact that triplet-triplet energy transfer from host aggregates to guest molecules. The fact that an unprecedented low guest-to-host ratio of 10 ppb still induces observable RTP indicates the new physical potential of multiple-component organic optoelectronic materials and calls for more state-of-the-art characterization and exploration.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: binary doping system • host and guest • parts-per-billion • room temperature phosphorescence • *sp*^{3} linked donor-acceptor

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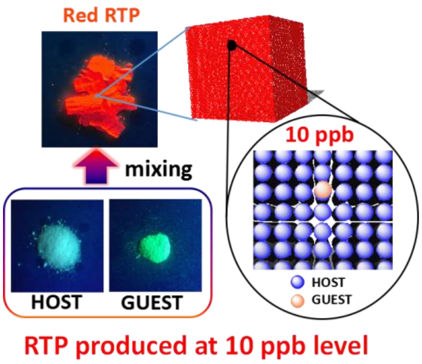

Red RTP is realized via doping at a guest-to-host ratio at the 10-parts-per-billion (ppb) level.