Molecular-Level Understanding of Dual-RTP via Host-Sensitized Multiple Triplet-to-Triplet Energy Transfers and Data Security Application

Nirmalya Acharya, Suvendu Dey, Raktim Deka, and Debdas Ray*

ABSTRACT: Dual-room-temperature phosphorescence (DRTP) from organic molecules is of utmost importance in chemical physics. The Dexter-type triplet-to-triplet energy transfer mechanism can therefore be used to achieve DRTP at ambient conditions. Here, we report two donor–acceptor (D–A)-based guests (CQN1, CQN2) in which the donor (D) and acceptor (A) parts are held in angular orientation around the C–N single bond. Spectroscopic analysis along with computational calculations revealed that both guests are incapable of emitting either thermally activated delayed fluorescence (TADF) or RTP at ambient conditions due to large singlet–triplet gaps, which are presented to show host (benzophenone, BP)-sensitized DRTP via multiple intermolecular triplet-to-triplet energy transfer (TTET) channels that originate from the triplet state (T1(D)) of BP to the triplet states (T1(D), T1(A)) of the D and A parts (TTET-I:T1(D) → T1(A); TTET-II:T1(D) → T1(A)). In addition, an intramolecular TTET channel that occurs from the T1(D) to T1(A) states of the D and A parts of CQN2 is also activated due to the low triplet (T1(D)–triplet (T1(A)) gap at ambient conditions. The efficiency of TTET processes was found to be 100%. The phosphorescence quantum yields (P) and lifetimes (τP) were shown to be 13–20% and 0.48–0.55 s, respectively. Given the high lifetime of the DRTP feature of both host–guest systems (1000:1 molar ratio), a data security application is achieved. This design principle provides the first solid proof that DRTP via radiative decay of the dark triplet states of the D and A parts of D–A-based non-TADF systems is possible, revealing a method to increase the efficiency and lifetime of DRTP.

INTRODUCTION

Room-temperature phosphorescent (RTP) materials shed light on the development of anticounterfeiting, information storage,1−4 and biological imaging5,6 due to the involvement of long-lived triplet emission. Generally, heavy metal-based inorganic systems are used because of strong spin–orbit coupling (SOC) induced by the heavy metals, which is conducive to high-efficiency RTP.7,8 However, these systems suffer from high costs and harsh preparation conditions, which limit their applications. Compared to their well-developed inorganic counterparts, organic RTP materials also have flourished due to their advantages of structural versatility and processability.9−14 However, most RTP materials show extremely dim photoluminescence because of weak SOC and their high sensitivity to temperature, moisture, and molecular oxygen.15 In this context, several rational strategies have been demonstrated to achieve efficient SOC including heavy atom effect,15−17 El-Sayed’s rule,18 and energy gap principle.3−5,18 In addition, host–guest systems,2,19−21 introducing intermolecular interactions,4,12,22−26 and rigid single crystals27−31 have also been established to suppress significant radiationless decays (kν) via rigidification of the emitter. However, these strategies still suffer from low phosphorescence quantum yield (Pν), and the obstacles of RTP seem impossible to be solved.

On the other hand, achieving dual-RTP (DRTP) via simultaneous radiative decay of T1 and T2 states (breakdown of Kasha’s rule) to the ground state (S0) is a challenging task in chemical physics. A handful of reports have established that the DRTP feature can be obtained by radiative decay of both T1 and T2 (vibronically mixed or thermally equilibrated from T1 state) states to the ground S0 state due to the low S1–T2 gap and faster ISC rates for S1 → T2 compared to S1 → T1.3,12−16,32−36 Because of these herculean prerequisites, organic high-efficiency DRTP materials have remained largely unexplored in photophysics.

Triple-totriplet energy transfer (TTET), which plays a pivotal role in chemistry and biology,37−40 is a well-known photophysical process of exchanging both spin and energy between a pair of molecules or intramolecular fragments. From this aspect, the TTET process that occurs when the two exchanging parts locate at a short distance (<10 Å, one
molecule\(^{41}\) and release energy via Dexter-type channels could become an alternative and effective transition pathway for the generation and stabilization of triplet excitons. Recently, utilizing this concept, a few RTP systems based on intra- and/or intermolecular TTET have been developed.\(^{41-46}\) However, the exact mechanism of DRTP and its control and the specific design principles for DRTP are yet to be developed. Therefore, the development of conceptually new methods to boost the efficiency and increase the lifetime of organic DRTP materials is of pivotal importance from both a fundamental viewpoint and for production of high-efficiency organic electronic devices.

Herein, we propose a strategy for harvesting dark triplet states (as DRTP) of D and A components of D–A guests that show neither thermally activated delayed fluorescence (TADF) nor RTP due to a large intrinsic energy gap (\(\Delta E_{SF}\)) between the S\(_1\) and T\(_1\) states (Figure 1a). Benzophenone (BP) was selected as a triplet sensitizer (host) because (a) the low-lying T\(_1\) energy level (T\(_1\)) remains higher in energy as compared with the lowest triplet states (T\(_1\), T\(_1\)) of D and A parts, which can enable multiple TTET channels, (b) the moderate dipole moment (\(\mu = 2.95 \text{ D}\)) can reduce the S\(_{CT}\)-T\(_{1}\) gap due to stabilization of the 1CT state and trigger the spin-forbidden intersystem crossing (ISC) between 1CT and T\(_{1}^{D}\), and (c) due to the facility for solution processing.

Three carbazole-quinoline-based donor–acceptor (D–A) conjugates (CQN1, CQN2), in which the carbazole donor is covalently attached to the quinolinyl acceptor via a C–N single bond, were selected as guests considering that the energies of T\(_1^{D}\) and T\(_1^{A}\) are very close and/or lower compared with T\(_1^{BP}\) to avoid energy loss. Carbazole (Cz), acceptor (QCN), and a control compound (CQM) were used to prove the hypothesis (Figure 1b). We anticipate that efficient ISC can occur between a guest and host that can convert the photogenerated singlet excitons of D–A into low-lying T\(_1^{BP}\), generating efficient DRTP from T\(_1^{D}\) and T\(_1^{A}\) via multiple TTET processes (TTET-I: T\(_1^{BP}\) → T\(_1^{D}\); TTET-II: T\(_1^{BP}\) → T\(_1^{A}\); TTET-III: T\(_1^{D}\) → T\(_1^{A}\)). Experimental and quantum chemistry calculations revealed that both D–A guests with a spatial separation of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) only show fluorescence via radiative decay of the 1CT state due to large \(\Delta E_{SF}\) values (0.53 eV–0.59 eV). We found that both host–guest (HG) (1000:1, molar ratio) binary systems (CQN1/BP, CQN2/BP) show efficient DRTP at ambient conditions (CQN1/BP: \(\lambda_{ex} = 415 \text{ nm}, \tau_P = 194.53, 352.20 \text{ ms}, \phi_f = 13 \pm 1\%\); CQN2/BP: \(\lambda_{ex} = 390 \text{ nm}, \tau_P = 164.08, 322.41 \text{ ms}, \phi_f = 20 \pm 2\%\)) via radiative decay of both T\(_1^{D}\) and T\(_1^{A}\) components caused by multiple TTET processes (TTET-I, TTET-II, TTET-III), which otherwise was impossible to achieve without using a sensitizer at ambient conditions. Given the persistent luminescence characteristics of both HG systems, a data security application has been developed. These results imply the feasibility of using multiple TTET strategies to harvest dark triplet states of non-TADF systems and boost the efficiency and lifetime of DRTP at ambient conditions.

### RESULTS AND DISCUSSION

#### Single-Crystal X-ray Analysis.
SCXRD analyses (Figure 2) of both the guests reveal that the carbazolyl ring and aryl substituents attached to the C8 and C4 atoms of the quinolinyl moiety deviate from planarity (CQN1: \(-49.66(3)\)°, \(-108.04(4)\)°; CQN2: 56.50(2)°, 126.31(2)°) when viewed along the C(11)−N(2)−C(8)−C(9) and C(18)−C(17)−C(4)−C(3) atoms, respectively (Figure S13; Table S1). We also found in both guests that aryl substitution at position 2 of the quinolinyl moiety causes the aryl substituents to be out of plane with torsions of 165.94(3) and \(-171.07(1)\)°, respectively, when viewed along the C(24)−C(23)−C(2)−N(1) atoms. X-ray analysis of both guests unambiguously confirms our structural model where D and A parts are held in angular orientation conducive for spatial separation of HOMO and LUMO.

#### Cyclic Voltammetry Analysis.
To understand the redox behaviors of both guests, CV measurements and the estimation of the HOMO and LUMO of both guests and their individual donor (Cz) and acceptor (QCN) parts were undertaken. Table S3 and Figure S14 reveal that HOMO and LUMO energies are essentially consistent with the energy difference between the HOMO and LUMO levels of Cz and QCN (2.82 and 3.23 eV) as determined by CV data. The results suggest that the HOMO−LUMO gaps in both guests are determined by the HOMO and LUMO levels of the Cz and QCN parts, and energies are largely localized on the Cz and QCN parts of both...
the guests, which is fully consistent with the X-ray structures of both systems in which the donor and acceptor are held in an angular arrangement, indicating a spatial separation of HOMO and LUMO.

Computational Analysis. To obtain further insight into the excited states of both guests, DFT and TD-DFT calculations were performed in GAUSSIAN 09 D.01 at the BLYP/6-31G level of theory (see the Supporting Information). The calculations revealed that the highest occupied molecular orbitals (HOMOs) are predominantly localized on the carbazolyl rings, while the lowest unoccupied molecular orbitals (LUMOs) are distributed over the quinolinyl fragments of CQN1 and CQN2 (Figures S15 and S16). The calculations also suggest that the isosurfaces of S1 states of both guests are localized on the quinolinyl fragment with partial contribution from the N atom of the carbazolyl ring, while the corresponding isosurfaces of T1 states are predominantly delocalized over the quinolinyl ring and its phenyl substituents at C2 and C4 positions, respectively (Figures S17 and S18). Natural transition orbitals (NTO) analysis revealed that the S1 state of both systems shows a pronounced CT-excitation character, as the hole and electron wave functions are localized at the donor and the acceptor fragments, respectively (Figures S15 and S16). Moreover, the calculated energy differences between S1 and T1 states (ΔEST) were found to be 0.569 eV (CQN1) and 0.507 eV (CQN2), which ruled out the possibility of TADF in both guests (Figures S17 and S18). These results demonstrate that both CQN1 and CQN2 exhibit only radiative decay of S1 (1CT) states to enable fluorescence.

Absorption and Emission Characteristics in Solutions and Films. Ultraviolet-visible (UV–vis) absorption measurements of CQN1 and CQN2 in both solutions and 1,3-bis(N-carbazolyl)benzene (mCP) films (1 wt %) show absorption peaks at ∼320 to 330 and ∼370 to 425 nm, respectively (Figures 3a and S19a). The hypsochromic shift of the lower-energy band (370−425 nm) with increasing solvent polarity...
confirms the CT nature of the absorption band while the former band ($\pi-\pi^*$ transition) has no effect on the solvent polarity, which are in line with previous reports (Figures 3a and S19a). The higher-energy absorption bands (~285 to 330 nm) of both guests closely resemble their absorptions of individual D and A parts, which indicates that the new lower-energy CT absorption band is due to the D–A torsional motion. Likewise, positive solvatochromism effects with a broadband emission feature and nanosecond lifetimes in toluene solutions (CQN1: $\lambda_{ex} = 328$ nm; $\tau_\phi = 9.52$ ns) ensure that both guests possess significant CT (S1→T1) at the excited state (fluorescence quantum yield, $\phi_F = \sim 25$ to $30\%$) (Figures 3a, S19b, and S20, Table 1). A similar fluorescence feature was also observed in mCP films ($\phi_{PL} = \sim 29$ to $36\%$) (Figure S21). To understand TADF, steady-state emission along with lifetime measurements of both conjugates in toluene solutions was carried out under oxygenated and degassed conditions at RT (Figures 3b,c and S22). We found that both conjugates show no significant change in the lifetime values (7.64–9.19 ns, degassed; 8.91–11.68 ns, oxygenated), proving that only radiative decay of 1CT states at ambient conditions is present. The phosphorescence measurement ($\lambda_{ex} = 328$ nm, 1.0 ms detector delay) at 77 K shows vibrational emission features ($0^1LE$) at 430–510, 560–580 (CQN1) nm, and 535–550 nm (CQN2), which closely overlaps with the phosphorescence peak of the D ($T_1^\pi$) (Cz) and A ($T_1^\pi$) part (QCN) of the guests (Figure 3d). It should be noted that D parts of both guests display phosphorescence (77 K) at ~495 nm, which was absent in the phosphorescence spectra of CQN2 due to an efficient intrinsic TTET-III ($T_1^\pi \rightarrow T_0^\pi$) channel compared to CQN1. The $\Delta E_{CT}$ values were calculated to be 0.53–0.59 eV, which rules out the possibility of TADF (Figure S23) and which is in good agreement with the computational analysis.

Absorption and Emission Characteristics of Host–Guest Binary Systems. Then, we systematically investigated the photophysical properties of the host and both HG binary systems that were prepared by solution processing with a H/G molar ratio of 1000:1. The absorption spectra of both HG systems showed similar absorption features (320–330, 370–430 nm) as those of CQN1, CQN2 (toluene and 1 wt % mCP film), and BP (Figures 4a and S24). Likewise, the steady-state emission ($\lambda_{ex} = 425$ nm, CQN1/BP; $\lambda_{ex} = 370$ nm, CQN2/BP) at ambient conditions shows bathochromically shifted emission peaks at 485 and 480 nm with a broad shoulder at 510–700 and 500–660 nm, respectively ($\phi_{PL} = \sim 23$ to $28\%$) (Figure 4b, Table 1). The parent emission peaks (485 and 480 nm) are assigned to the fluorescence (broad, S1→T1) and are confirmed in the fluorescence decay measurement ($\tau_\phi = 10.45$ and 12.56 ns) (Figure S25).

To investigate DRTP, phosphorescence measurements (1.0 ms detector delay) were performed at ambient conditions. Interestingly, both HG systems exhibit DRTP features (CQN1/BP: $\lambda_{ex} = 425$ nm, $\Phi_F = 226.10$ ms; $\lambda_{ex} = 415$ nm, $\Phi_F = 218.67$ ms; $\lambda_{ex} = 370$ nm, $\Phi_F = 378.42$ ms; $\lambda_{ex} = 390$ nm, a greenish-yellow and yellow-orange afterglow that can be directly observed with the naked eye (Figures 4b,d and S26, Tables 1 and S4)). Further, a continuous increase in the lifetime of both emission bands upon lowering of the temperature (300–10 K) (Figures 4c,d, S26, and Table S4) confirms that both HG systems show DRTP via radiative decay of two excited triplet states.

Temperature-Dependent Time-Resolved Emission Spectra (TRES) Analysis of Binary Systems. To obtain further insight into exciton dynamics, temperature-dependent (300–10 K) TRES measurements were carried out (Figures 5 and S27–S31). At 300 K, the emission bands of both HG systems ($\lambda_{ex} = 425$ nm, CQN1; $\lambda_{ex} = 370$ nm, CQN2) show a gradual bathochromic shift at time delays of 1.5–6.5 ns. No further red shift was observed after a time delay of 6.5 ns. At

| Table 1. Photophysical Parameters of CQN1, CQN2, CQN1/BP, CQN2/BP, and BP |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| sample         | $\lambda_{ex}$ (nm) | $\tau_\phi$ (ns) | $\phi_{PL}$ (%) | $\Delta E_{CT}$(eV) | $\Delta E_{TT}$ (eV) |
| BP             | 445              | 7.86            | 25 ± 2          | 0.59 (S1→T1)     | 0.07 (T1→T1)     |
| CQN1           | 489              | 9.52            | 30 ± 1          | 0.53 (S1→T1)     | 0.36 (T1→T1)     |
| CQN2           | 483              | 10.45           | 10 ± 2          | 0.50 (1CT→T1)    | 0.29 (T1→T1)     |
| CQN1/BP        | 495              | 194.53          | 13 ± 1          | 0.21 (1CT→T1)    | 0.29 (T1→T1)     |
| CQN2/BP        | 560              | 352.20          |                | 0.51 (1CT→T1)    | 0.07 (T1→T1)     |
| CQN2/BP        | 540              | 495             | 20 ± 2          | 0.22 (1CT→T1)    | 0.22 (T1→T1)     |

* $\lambda_{ex} = 320$ and 328 nm. *Average lifetimes. *Quantum yields of fluorescence and phosphorescence. *Singlet–triplet and triplet–triplet energy gaps.
10, 77, and 150 K, the emission dynamics of both HG systems remain almost the same, indicating that a singlet charge transfer state (S1\(\rightarrow\) CT) is responsible for the emission (Figures S27 and S28). To investigate TTET, TRES measurements were undertaken at different delays with varying temperatures.

At 300 K, a dual emission feature (CQN1/BP: \(\lambda_{em} = 495\), 560 nm; \(\lambda_{em} = 415\) nm) was recorded at a delay time of 0.23 s, which remained unchanged during the delay time of 0.23–0.37 s (Figure 5a). Surprisingly, at 150 K, a similar delay time (0.23 s) resulted in two clearly located excitations (LE1: ~455 to 500 nm; LE2: ~S10 to 715 nm); the former LE1 has higher on-set energy as compared with the broad emission band observed at 495 nm at RT, indicating a new higher-energy local triplet (\(T_{1D}^{BP}\)) state that enables TTET-II (Figures 5b and S32a) at RT. After a 0.25 s delay, a significant decrease in the intensity of LE1 with an increase in the intensity of LE2 was observed during delays of 0.25–0.37 s, showing efficient TTET-II via \(T_{1D}^{BP} \rightarrow T_{1A}\) (Figure 5a). Further, at 10–77 K with the same delays (0.23–0.37 s), emission features from both LE1 (\(T_{1D}^{BP}\)) and LE2 (\(T_{1A}\)) along with donor emission (\(T_{1}\)CQN1/BP, 495 nm) (submerged with LE1) are observed, ensuring inefficient TTET (Figures 5c and 29a).

On the other hand, Figures S29b, S31, and S5d–f represent the emission profiles of long-lived (ms) components of the emission decays of CQN2/BP at 10–300 K. At 300 K, we found a similar dual emission feature (CQN2/BP: \(\lambda_{em} = 495\), 540 nm; \(\lambda_{em} = 390\) nm) in a delay time of 0.23 s, except that a significant reduction in the intensity of the higher-energy emission band (495 nm) as compared with CQN1/BP was recorded. At a further delay of 0.27–0.37 s, no bathochromic shift of the emission bands was observed. At 150 K, two clear LE features (LE1: 495 nm; LE2: 540 nm) were observed. Interestingly, the energy on-set of LE1 is lower in energy than that of LE1 of CQN1/BP (Figure S32b), indicating that contribution of LE1 of CQN2/BP is due to radiative decay of \(T_{1}\)CQN2/BP. Later time scales of 0.27–0.37 s resulted in no shift of the emission bands. However, a significant reduction in the intensity of the higher-energy emission band (LE1) with an increase in the intensity of the lower-energy emission band (LE2) was observed at time delays of 0.27–0.37 s, which is consistent with that of CQN1/BP. These results suggest that both TTET-I (via \(T_{1A}^{BP} \rightarrow T_{1D}^{BP}\)) and TTET-II (via \(T_{1A}^{BP} \rightarrow T_{1A}\)) are also activated in CQN2/BP. At 77–10 K, no significant TTET processes occur as predominant emission contribution from LE1 (\(T_{1D}^{BP}\)) and LE2 (\(T_{1A}\)) is clearly visible in the TRES measurements. It should be noted that TTET-I (\(T_{1A}^{BP} \rightarrow T_{1D}^{BP}\)) in CQN1/BP is activated at 300 K while CQN2/BP exhibits efficient TTET-I at 150 K. Since most of the emissive photons arise from the long-lived \(T_{1A}\) (\(\tau_{p} = 322.41\) ms, RT), we speculate that an additional TTET-III channel has been activated in CQN2/BP, which is responsible for efficient DRTP as compared with CQN1/BP (Figures 4b and S32b). To understand TTET-III, we performed temperature-dependent (77, 10 K) phosphorescence measurements of both guests. At 77 and 10 K, both guests exhibit dual phosphorescence bands (CQN1: 495, 560 nm; CQN2: 495, 540 nm) due to radiative decay of \(T_{1A}\) and \(T_{1D}\) (Figure S33). Interestingly, CQN2 on increasing the temperature from 10 to 77 K shows a decrease in intensity of the higher-energy local emission band (495 nm) with an increase in the intensity of the lower-energy local emission band (540 nm), while a significant reduction in the intensity of both local triplets (\(T_{1A}, T_{1D}\)) of CQN1 was observed. These observations clearly confirm that an efficient intrinsic TTET-III process is activated in CQN2. It should be noted that no significant change in the emission dynamics of both the HG systems was observed when higher-energy photoexcitation (328 nm) was used in the TRES measurements (Figures S30 and S31).

**Energy Gap Analysis.** Energy gaps were calculated to be 0.21–0.33 (\(\Delta E_{S_{1CT} \rightarrow T_{1D}}\)), 0.07 (\(\Delta E_{T_{1D}^{BP} \rightarrow T_{1A}}\)), 0.29–0.36 (\(\Delta E_{T_{1A}^{BP} \rightarrow T_{1A}}\)), and 0.22–0.29 (\(\Delta E_{T_{1A} \rightarrow T_{1D}}\)) eV, respectively, considering the onset of the steady-state emission spectra and emission maximums of the phosphorescence spectra (1.0 ms detector delay, RT) recorded at 300 K (Figure S34, Tables 1 and S5). The low energy gap (\(\Delta E_{S_{1CT} \rightarrow T_{1D}}\)) suggests that an efficient ISC occurs from \(S_{1CT}\) to \(T_{1D}\), which further triggers TTET-I and TTET-II channels due to the close proximity of \(T_{1D}, T_{1A}\), and \(T_{1D}\). Further, a low \(T_{1D} - T_{1A}\) gap of 0.22 eV in CQN2/BP as compared with CQN1/BP (0.29 eV) ensures that an additional TTET-III process is activated at and above 77 K. Since we observed TTET-I at 150 K in CQN2/BP (see Figure 5. Delay-dependent TRES of CQN1/BP (\(\lambda_{em} = 415\) nm) at (a) 300 K, (b) 150 K, and (c) 10 K. Delay-dependent TRES of CQN2/BP at (d) 300 K, (e) 150 K, and (f) 10 K (\(\lambda_{em} = 390\) nm).
TRESS analysis discussed before), we anticipate that TTET-III may further be triggered to activate TTET-I at 150 K, while TTET-I is activated in CQN1/BP at 300 K, which can be explained by the relatively low $T_{1D}^D - T_{1A}^D$ gap of CQN2/BP as compared with that of CQN1/BP. Considering low $\Delta E_{T1CT}^{CT} - T1D^D$, $\Delta E_{T1CT}^{CT} - T1A^A$, and $\Delta E_{T1CT}^{CT} - T1P^P$ values, and high $\phi_P$ and $\tau_P$ values of CQN2/BP as compared with CQN1/BP, we conclude that CQN2/BP exhibits efficient DRTP with minimal energy loss via multiple TTET channels (Figures 6 and S34). Based on these results, we believe that both guests show DRTP due to the host-sensitized multiple TTETs.

**Excitation-Dependent Emission and Excitation Spectra Analysis.** To obtain further insight into the emission dynamics, excitation-dependent emission measurements were performed at RT. When we excite both the HG systems at 320 nm, no change in the steady-state emission feature as compared with the steady-state emission recorded at excitation of 425 nm (CQN1/BP) and 370 nm (CQN2/BP) (Figures 4b and S35) is observed. On the other hand, RTP measurements (1.0 ms detector delay) with photoexcitation of 328 nm for both HG systems resulted in a dual-RTP feature, which is fully consistent with the dual-RTP feature recorded at excitations of 415 nm (CQN1/BP) and 390 nm (CQN2/BP) (Figures 4b and S36). These results suggest that no excitation-dependent emission characteristics are involved in the emission of both HG systems. Further, to understand ground- and excited-state heterogeneities of both HG systems, excitation spectra were recorded at RT and 77 K. Excitation spectra measurements while monitoring the emission wavelengths of 487 nm (CQN1/BP) and 480 nm (CQN2/BP) at RT (steady-state spectra) revealed that lower-energy regions (CQN1/BP: 390–475 nm; CQN12BP: 365–450 nm) of the excitation spectra closely overlap with the lower-energy region of the absorption spectra of CQN1/BP and CQN2 BP, while the higher-energy regions (CQN1/BP: 285–390 nm; CQN2/BP: 285–365 nm) of the excitation spectra overlap with the higher-energy regions of the absorption spectra of CQN1/BP, CQN2/BP, and BP (Figure S37). Phosphorescence excitation spectra of both HG systems at RT also revealed similar absorption features as those of steady-state excitation spectra at RT (Figure S38). It should be noted that both HG systems in phosphorescence measurements (1.0 ms detector delay) at 77 K resulted in dominant LE emission bands at 480 nm, which originate from the host (T1D). When we compare the excitation spectra of BP recorded at RT with the excitation spectra of CQN1/BP and CQN2/BP at 77 K while monitoring the LE emission band of BP (480 nm), it is observed that both excitation spectra are closely overlapped with each other. These results ensure that no heterogeneity is present in both the ground and excited states. Since phosphorescence emission contribution (excitation independent) from BP in both HG systems is absent, we confirm that 100% sensitization has occurred from T1D to T1P and T1A of the guests (CQN1, CQN2), proving host-sensitized multiple TTETs that triggers DRTP at ambient conditions.

**Control Analysis.** To test our hypothesis, we synthesized CQM (see the Supporting Information), in which the C2 and C4 positions of the quinolinyl core are substituted by phenyl rings while the methyl group is introduced at the C5 position inducing an electronic effect. The PL measurements show that CQM also exhibits fluorescence both in solutions and solid state via radiative decay of the $S1CT$ (445 nm) state, which is hypsochromically shifted as compared with the other guests, indicating that $S1CT$ has higher energy as compared to the $S1CT$ and $T1CT$ states of BP (Figure S39). The large $\Delta ST$ value ($\Delta E_{S1CT,T1D} = 0.58$ eV) like other guests eliminates the possibility of TADF. Since CQM/BP with the same molar ratio resulted in no RTP/DRTP features ($\lambda_{ex} = 328$ nm) at RT, we confirm that TTET is not activated due to an inefficient ISC from $S1CT$ to $T1BP$. Therefore, we conclude that $T1D$ of the host, which falls between $S1CT$ and $T1P$ and/or $T1A$ of guests, can enable multiple TTETs that are responsible for DRTP of CQN1 and CQN2 at ambient conditions (Figure 6).

**Discussion.** Both guest molecules showed no thermally activated delayed fluorescence (TADF) due to high $S1T - T1D$ gaps; only radiative decay of excited singlet states ($1CT$) was observed both in solutions and solid states. A comparison between the PL analysis of guests (CQN1, CQN2) and host–guest (HG) systems (CQN1/BP, CQN2/BP) suggests that the higher-energy triplet state of the host ($T1BP$) sensitizes lower-energy triplet states ($T1P$, $T1A$) of guests in the HG binary systems leading to dual-RTP at ambient conditions via multiple triplet-to-triplet energy transfer (TTET) channels. Further, a comparison between the excitation-dependent emission analysis of both HG systems recorded at RT and 77 K ensures that multiple TTET channels are activated at RT, proving DRTP at ambient conditions. Further, when
comparing the excitation and absorption spectra of the HG systems, we confirm that dual-RTP with an afterglow (CQN1/ BP; \( \lambda_{495} \), \( \tau_p = 226.10, 118.42 \text{ ms}; \lambda_{660} \), \( \tau_p = 412.85, 208.61 \text{ ms}; \) CQN2/BP; \( \lambda_{495} \), \( \tau_p = 186.76, 88.51 \text{ ms}; \lambda_{640} \), \( \tau_p = 378.42, 237.75 \text{ ms} \)) feature originated due to host-sensitized multiple TTETs in the excited states. Such host-sensitized RTP with an afterglow feature is reported in the literature, where the triplet state of the host plays an important role to sensitize the closely spaced triplet state of the guest in the excited states.

The emission analysis of both guests and HG systems reported here indicates that the intramolecular TTET (TTET-III) is also activated in CQN2/BP along with the intermolecular TTET (TTET-I, TTET-II) due to close energy gaps (\( T_2^0 - T_1^0 \)) between the donor and acceptor components, which provides an additional driving force to alter the DRTP feature. When comparing the phosphorescence analysis of both HG systems, we found that the intensity of the lower-energy RTP band (excitation independent) in CQN2/BP is significantly higher as compared with CQN1/BP. Therefore, different DRTP properties of both the HG systems can be explained by the low intrinsic \( T_1^0 - T_1^0 \) gap of 0.22 eV in CQN2 as compared with CQN1 (0.29 eV). Comparison of the phosphorescence bands of the respective guests and their HG systems recorded at 77 and 300 K along with absorption and excitation spectra analysis (Figures S37, S38, and S40) ruled out the possibility of ground-state and excited-state heterogeneities present in the HG systems. Furthermore, it is established that the benzophenone host plays an important role in (a) maintaining rigidity, (b) reducing nonradiative pathways (\( k_{nr} \), \( k_{nr} \)), and (c) increasing the lifetime of the triplet states. \(^{3,44} \) We ensure that the triplet state (\( T_1^0 \)) of benzophenone enables intermolecular TTETs leading to efficient dual-RTP with an afterglow feature under ambient conditions. These results demonstrate that a careful section of the triplet state of the host plays an important role in populating the triplet states of donor and acceptor parts of non-TADF systems, setting a benchmark for achieving dual-RTP with an afterglow feature via host-sensitized multiple TTETs (Figure 6).

**Data Security Applications.** Given the afterglow (CQN1/BP; \( \lambda_{495} \), \( \tau_p = 118–226 \text{ ms}; \lambda_{660} \), \( \tau_p = 208–413 \text{ ms} \); CQN2/BP; \( \lambda_{495} \), \( \tau_p = 88–187 \text{ ms}; \lambda_{640} \), \( \tau_p = 237–379 \text{ ms} \)) feature of both HG systems, we have developed a security pattern of \( V \) made of CQN1 and CQN1/BP and CQN2 and CQN2/BP. To achieve host–guest binary systems for data security applications, we dissolved both the host (H) and guest (G) (1000:1 molar ratio) in dichloromethane (DCM) solutions. The solution was drop-cast on a glass plate and evaporated under slow heating conditions (40 °C). To demonstrate data security applications, we utilized the same HG binary systems on ordinary black paper. The symbol “V” was written using CQN1 with CQN1/BP and CQN2 with CQN2/BP was written (Figure 7) separately. A cyan-blue pattern of “V” was observed after irradiation with a UV lamp (365 nm). Switching off the lamp resulted in green and yellow patterns of “V” encrypted by CQN1/BP and CQN2/BP, respectively, due to the absence of the afterglow property of the guest itself (web-enhanced objects 1, 2). Thus, application of anticounterfeiting and information storage is achievable using these simple systems.

**CONCLUSIONS**

To conclude, the first example of efficient DRTP via multiple triplet-to-triplet energy transfers (TTETs) is presented here.
from Agilent Technologies. Steady-state emission, phosphorescence, and lifetime analysis of the samples were recorded on Horiba Fluorolog-3 and Edinburgh FLS980 spectrometers. All of the phosphorescence spectra were recorded using a detector delay of more than 0.5 ms. The measurement details can be found in the reported literature.9−11,14,18 Temperature-dependent PL measurements were performed using a cryostat (JANIS CS204SE-FMX-1AL). Cyclic voltammetry was performed using a BioLogic potentiostat. The electrochemical cell included a glassy carbon disk as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo thermogravimetric analyzer (TGA2 SP/1100: RT to 800 °C). High-performance liquid chromatography (HPLC) experiments were carried out on a Waters Alliance system (Milford, MA) consisting of an e2695 separation module and a 2998 photodiode-array detector.

■ SUPPORTING INFORMATION

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06390.

Experimental procedures; NMR spectra of all compounds; high-performance liquid chromatography; single-crystal X-ray diffraction analysis; UV−vis absorption spectra; steady-state emission; time-correlated single photon counting measurement; phosphorescence spectra; temperature-dependent time-resolved emission spectra; cyclic voltammetry; thermogravimetric analysis; quantum yields; rate parameters; and computational details (PDF)

Crystallographic data for CQN1 (CIF)
Crystallographic data for CQN2 (CIF)
Crystallographic data for CQM (CIF)
(avi)

■ AUTHOR INFORMATION

Corresponding Author
Debdas Ray − Advanced Photofunctional Materials Laboratory, Department of Chemistry, Shiv Nadar University, Tehsil Dadri, Uttar Pradesh 201314, India; orcid.org/0000-0002-6169-8823; Email: debdas.ray@snu.edu.in

Authors
Nirmalya Acharya − Advanced Photofunctional Materials Laboratory, Department of Chemistry, Shiv Nadar University, Tehsil Dadri, Uttar Pradesh 201314, India
Suvendu Dey − Advanced Photofunctional Materials Laboratory, Department of Chemistry, Shiv Nadar University, Tehsil Dadri, Uttar Pradesh 201314, India
Raktim Deka − Advanced Photofunctional Materials Laboratory, Department of Chemistry, Shiv Nadar University, Tehsil Dadri, Uttar Pradesh 201314, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06390

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.R. is grateful to the Science and Engineering Research Board (SERB) (File No: EEQ/2020/ 000029), DST, and Shiv Nadar University (SNU) for their generous support. N.A., S.D., and R.D. thank SNU for the fellowship. The authors thankfully acknowledge the use of the MAGUS supercomputing system at SNU.

■ REFERENCES

(1) Xu, S.; Chen, R.; Zheng, C.; Huang, W. Excited State Modulation for Organic Afterglow: Materials and Applications. Adv. Mater. 2016, 28, 9920−9940.
(2) Hirata, S. Recent Advances in Materials with Room-Temperature Phosphorescence: Photophysics for Triplet Exciton Stabilization. Adv. Opt. Mater. 2017, 5, No. 1700116.
(3) Bhattacharjee, I.; Ray, D. Use of Dimeric Excited States of the Donors in D−A Systems for Accessing White Light Emission, Afterglow, and Invisible Security Ink. J. Phys. Chem. C 2019, 123, 22104−22113.
(4) Bhattacharjee, I.; Ray, D. Biluminescence Via Fluorescence and Persistent Phosphorescence in Amorphous Organic Donor (D)−Acceptor (A) Conjugates and Application in Data Security Protection. J. Phys. Chem. Lett. 2018, 9, 3808−3813.
(5) Zhang, G.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. L. A Dual-Emissive-Materials Design Concept Enables Tumour Hypoxia Imaging. Nat. Mater. 2009, 8, 747−751.
(6) Yang, J.; Zhang, Y.; Wu, X.; Dai, W.; Chen, D.; Shi, J.; Tong, B.; Peng, Q.; Xie, H.; Cai, Z. Rational Design of Pyrrole Derivatives with Aggregation-Induced Phosphorescence Characteristics for Time-Resolved and Two-Photon Luminescence Imaging. Nat. Commun. 2021, 12, No. 4883.
(7) Turro, N. J.; Ramamurthy, V.; Ramamurthy, V.; Scaiano, J. C. Principles of Molecular Photochemistry: An Introduction; University Science Books, 2009.
(8) Baldo, M. A.; O’Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices. Nature 1998, 395, 151−154.
(9) Bhattacharjee, I.; Acharya, N.; Ray, D. Thermally Activated Delayed Fluorescence and Room-Temperature Phosphorescence in Naphthyl Appended Carbazole−Quinoline Conjugates, and Their Mechanical Regulation. Chem. Commun. 2019, 55, 1899−1902.
(10) Bhattacharjee, I.; Acharya, N.; Bhatia, H.; Ray, D. Dual Emission through Thermally Activated Delayed Fluorescence and Room-Temperature Phosphorescence, and Their Thermal Enhancement Via Solid-State Structural Change in a Carbazole-Quinoline Conjugate. J. Phys. Chem. Lett. 2018, 9, 2733−2738.
(11) Bhatia, H.; Ray, D. Asymmetric-Donor (D2D2′−Acceptor (A) Conjugates for Simultaneously Accessing Intrinsic Blue-RTF and Blue-TADF. Mater. Adv. 2020, 1, 1858−1865.
(12) Bhatia, H.; Dey, S.; Ray, D. Effect of π−π Interactions of Donor Rings on Persistent Room-Temperature Phosphorescence in D−A Conjugates and Data Security Application. ACS Omega 2021, 6, 3858−3865.
(13) Alam, P.; Leung, N. L.; Liu, J.; Cheung, T. S.; Zhang, X.; He, Z.; Kwok, R. T.; Lam, J. W.; Sung, H. H.; Williams, I. D.; et al. Two Are Better Than One: A Design Principle for Ultralong-Persistent Luminescence of Pure Organics. Adv. Mater. 2020, 32, No. 2001026.
(14) Acharya, N.; Hasan, M.; Dey, S.; Lo, S.-C.; Namdas, E. B.; Ray, D. Phenothiazine−Quinoline Conjugates Realizing Intrinsic Thermally Activated Delayed Fluorescence and Room-Temperature Phosphorescence: Understanding the Mechanism and Electro-luminescence Devices. Adv. Photon. Res. 2021, 2, No. 2000201.
(15) Khudyakov, I. V.; Serebrennikov, Y. A.; Turro, N. J. Spin-Orbit Coupling in Free-Radical Reactions: On the Way to Heavy Elements. Chem. Rev. 1993, 93, 537−570.
(16) Lower, S.; El-Sayed, M. The Triplet State and Molecular Electronic Processes in Organic Molecules. Chem. Rev. 1966, 66, 199−241.
(17) El-Sayed, M. Spin-Orbit Coupling and the Radiationless Processes in Nitrogen Heterocyclics. J. Chem. Phys. 1963, 38, 2834–2838.

(18) Bhattacharjee, I.; Acharya, N.; Karmakar, S.; Ray, D. Room-Temperature Orange-Red Phosphorescence by Way of Intermolecular Charge Transfer in Single-Component Phenoxazine–Quinoline Conjugates and Chemical Sensing. J. Phys. Chem. C 2018, 122, 21589–21597.

(19) Notsuka, N.; Kabe, R.; Goushi, K.; Adachi, C. Confinement of Long-Lived Triplet Excitons in Organic Semiconductor Host–Guest Systems. Adv. Funct. Mater. 2017, 27, No. 1703902.

(20) Bhattacharjee, I.; Hirata, S. Highly Efficient Persistent Room-Temperature Phosphorescence from Heavy Atom-Free Molecules Triggered by Hidden Long Phosphorescent Antenna. Adv. Mater. 2020, 32, No. 2001348.

(21) Bhattacharjee, I.; Hayashi, K.; Hirata, S. Key of Suppressed Triplet Nonradiative Transition-Dependent Chemical Backbone for Spatial Self-Tunable Afterglow. JACS Au 2021, 1, 945–954.

(22) Yang, J.; Zhen, X.; Wang, B.; Gao, X.; Ren, Z.; Wang, J.; Xie, Y.; Li, J.; Peng, Q.; Pu, K. The Influence of the Molecular Packing on the Room Temperature Phosphorescence of Purely Organic Luminogens. Nat. Commun. 2018, 9, No. 840.

(23) Wen, Y.; Liu, H.; Zang, S.; Gao, Y.; Yan, Y.; Yang, B. One-Dimensional II–II Stacking Induces Highly Efficient Pure Organic Room-Temperature Phosphorescence and Ternary-Emission Single-Molecule White Light. J. Mater. Chem. C 2019, 7, 12502–12508.

(24) Liu, W.; Wang, J.; Gong, Y.; Liao, Q.; Dang, Q.; Li, Z.; Bo, Z. Room-Temperature Phosphorescence Invoked through Norbornyl-Driven Intermolecular Interaction Intensification with Anomalous Reversible Solid-State Photochromism. Angew. Chem., Int. Ed. 2020, 59, 20161–20166.

(25) Gan, N.; Wang, X.; Ma, H.; Lv, A.; Wang, H.; Wang, Q.; Gu, M.; Cai, S.; Zhang, Y.; Fu, L.; et al. Manipulating the Stacking of Triplet Molecules in the Crystal Form for Ultralong Organic Phosphorescence. Angew. Chem., Int. Ed. 2019, 58, 14140–14145.

(26) Chai, Z.; Wang, C.; Wang, J.; Liu, F.; Xie, Y.; Zhang, Y.-Z.; Li, J.-R.; Li, Q.; Li, Z. Abnormal Room Temperature Phosphorescence of Purely Organic Boron-Containing Compounds: The Relationship between the Emissive Behavior and the Molecular Packing, and the Potential Related Applications. Chem. Sci. 2017, 8, 8336–8344.

(27) Yuan, W. Z.; Zhen, X. Y.; Zhao, H.; Lam, J. W.; Tang, L.; Lu, P.; Wang, C.; Liu, Y.; Wang, Z.; Zheng, Q.; et al. Crystallization-Induced Phosphorescence of Pure Organic Lumogens at Room Temperature. J. Phys. Chem. C 2010, 114, 6090–6099.

(28) Yoshii, R.; Hirose, A.; Tanaka, K.; Chuo, Y. Functionalization of Boron Diminuates with Unique Optical Properties: Multicolor Tuning of Crystallization-Induced Emission and Introduction into the Main Chain of Conjugated Polymers. J. Am. Chem. Soc. 2014, 136, 18131–18139.

(29) He, G.; Du, L.; Gong, Y.; Liu, Y.; Yu, C.; Wei, C.; Yuan, W. Z. Crystallization-Induced Red Phosphorescence and Grinding-Induced Blue-Shifted Emission of a Benzobis (1, 2, 5-Thiadiazole)–Thiophene Conjugate. ACS Omega 2019, 4, 344–351.

(30) Gong, Y.; Zhao, L.; Peng, Q.; Fan, D.; Yuan, W. Z.; Zhang, Y.; Tang, B. Z. Crystallization-Induced Dual Emission from Metal-and Heavy Atom-Free Aromatic Acids and Esters. Chem. Sci. 2015, 6, 4438–4444.

(31) Bolton, O.; Lee, K.; Kim, H.-J.; Lin, K. Y.; Kim, J. Activating Efficient Phosphorescence from Purely Organic Materials by Crystal Design. Nat. Chem. 2011, 3, 205–210.

(32) Paul, L.; Moitra, T.; Ruud, K.; Chakrabarti, S. Strong Duschinsky Mixing Induced Breakdown of Kash’s Rule in an Organic Phosphor. J. Phys. Chem. Lett. 2019, 10, 369–374.

(33) Paul, L.; Chakrabarti, S.; Ruud, K. Anomalous Phosphorescence from an Organometallic White-Light Phosphor. J. Phys. Chem. Lett. 2017, 8, 4893–4897.

(34) Itoh, T.; Hashimoto, R. Temperature Dependence of the Emission Spectra of P-Benziquinoine in a P-Dichlorobenzene Matrix. J. Lumin. 2012, 132, 236–239.

(35) Itoh, T. Fluorescence and Phosphorescence from Higher Excited States of Organic Molecules. Chem. Rev. 2012, 112, 4541–4568.

(36) He, Z.; Zhao, W.; Lam, J. W.; Peng, Q.; Ma, H.; Liang, G.; Shuai, Z.; Tang, B. Z. White Light Emission from a Single Organic Molecule with Dual Phosphorescence at Room Temperature. Nat. Commun. 2017, 8, No. 416.

(37) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy Transfer Catalysis Mediated by Visible Light: Principles, Applications, Directions. Chem. Soc. Rev. 2018, 47, 7190–7202.

(38) Luo, X.; Han, Y.; Chen, Z.; Li, Y.; Liang, G.; Liu, X.; Ding, T.; Nie, C.; Wang, M.; Castellano, F. N.; et al. Mechanisms of Triplet Energy Transfer across the Inorganic Nanocrystal/Organic Molecule Interface. Nat. Commun. 2020, 11, No. 28.

(39) Jortner, J.; Choi, S.-I.; Katz, J. L.; Rice, S. A. Triplet Energy Transfer and Triplet-Triplet Interaction in Aromatic Crystals. Phys. Rev. Lett. 1963, 11, No. 323.

(40) Großkopf, J.; Kratz, T.; Rigotti, T.; Bach, T. Enantioselective Photophysical Reactions Enabled by Triplet Energy Transfer. Chem. Rev. 2021, DOI: 10.1021/acs.chemrev.1c00272.

(41) Zhao, W.; Cheung, T. S.; Jiang, N.; Huang, W.; Lam, J. W.; Zhang, X.; He, Z.; Tang, B. Z. Boosting the Efficiency of Organic Persistent Room-Temperature Phosphorescence by Intramolecular Triplet-Triplet Energy Transfer. Nat. Commun. 2019, 10, No. 1595.

(42) Xie, Z.; Zhang, X.; Wang, H.; Huang, C.; Sun, H.; Dong, M.; Ji, L.; An, Z.; Yu, T.; Huang, W. Wide-Range Lifetime-Tunable and Responsive Ultralong Organic Phosphorescent Multi-Host/Guest System. Nat. Commun. 2021, 12, No. 3522.

(43) Wang, D.; Xie, Y.; Wu, X.; Lei, Y.; Zhou, Y.; Cai, Z.; Liu, M.; Wu, H.; Huang, X.; Dong, Y. Excitation-Dependent Triplet–Singlet Intensity from Organic Host–Guest Materials: Tunable Color, White-Light Emission, and Room-Temperature Phosphorescence. J. Phys. Chem. Lett. 2021, 12, 1814–1821.

(44) Qiu, W.; Cai, X.; Li, M.; Chen, Z.; Wang, L.; Xie, W.; Liu; K.; Liu, M.; Su, S.-J. Achieving Purely Organic Room-Temperature Phosphorescence Mediated by a Host–Guest Charge Transfer State. J. Phys. Chem. Lett. 2021, 12, 4600–4608.

(45) Liu, Y.; Li, Y.; Wen, Y.; Su, X.; Xu, M.; Feng, W.; Liu, Q.; Li, F. Significantly Enhanced Afterglow Brightness Via Intramolecular Energy Transfer. ACS Mater. Lett. 2021, 3, 713–720.

(46) Lei, Y.; Yang, J.; Dai, W.; Lan, Y.; Yang, J.; Zheng, X.; Shi, J.; Tong, B.; Cai, Z.; Dong, Y. Efficient and Organic Host–Guest Room-Temperature Phosphorescence: Tunable Triplet–Singlet Crossing and Theoretical Calculations for Molecular Packing. Chem. Sci. 2021, 12, 6518–6525.

(47) Runge, E.; Gross, E. K. Density-Functional Theory for Time-Dependent Systems. Phys. Rev. Lett. 1984, 52, No. 997.

(48) Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.. Energy Transfer Catalysis Mediated by Visible Light: Principles, Applications, Directions. Chem. Soc. Rev. 2018, 47, 7190–7202.

(49) Itoh, T.; Hashimoto, R. Temperature Dependence of the Emission Spectra of P-Benziquinoine in a P-Dichlorobenzene Matrix. J. Lumin. 2012, 132, 236–239.