Evidence and mechanism of efficient thermally activated delayed fluorescence promoted by delocalized excited states

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The design of organic compounds with nearly no gap between the first excited singlet (S1) and triplet (T1) states has been demonstrated to result in an efficient spin-flip transition from the T1 to S1 state, that is, reverse intersystem crossing (RISC), and facilitate light emission as thermally activated delayed fluorescence (TADF). However, RISC molecules have shown that a relatively appreciable energy difference between the S1 and T1 states (~0.2 eV) could also result in a high RISC rate. We revealed from a comprehensive study of optical properties of TADF molecules that the formation of delocalized states is the key to efficient RISC and identified a chemical template for these materials. In addition, simple structural confinement further enhances RISC by suppressing structural relaxation in the triplet states. Our findings aid in designing advanced organic molecules with a high rate of RISC and, thus, achieving the maximum theoretical electroluminescence efficiency in organic light-emitting diodes.

INTRODUCTION

One of the most effective ways to enhance internal electroluminescence (EL) quantum efficiency (ηint) in organic light-emitting diodes (OLEDs) is well recognized to be the management of the pathways between excited singlet (S) and triplet (T) states. In OLEDs, the effective use of triplets is fundamental for achieving high ηint, because one singlet is generated for every three triplets based on spin statistics under electrical excitation (Fig. 1A) (1). Although a spin–flip from pure S to pure T states, that is, intersystem crossing (ISC), is generally forbidden because of their different spin multiplicities, it becomes possible when their wave functions are mixed through spin-orbital coupling (SOC). The degree of mixing (λ) can be simply expressed as λ = HSO/ΔE_ST, where HSO and ΔE_ST are the SOC constant and energy difference between the S1 and T1 states, respectively (2). By incorporating a heavy atom such as iridium into organic molecules, HSO is enhanced and a strong mixing of the spin orbitals of the S and T states is induced, resulting in efficient radiative decay from T1 to the ground state (S0), that is, phosphorescence, with nearly 100% of photoluminescence (PL) quantum yield (PLQY) (3).

Alternatively, the λ can be enhanced by decreasing ΔE_ST, which can also open a pathway from lower-energy T1 to higher-energy S1, that is, reverse ISC (RISC), when ΔE_ST is small enough. On the basis of quantum chemical theory, ΔE_ST is proportional to the exchange energy, which is related to the overlap integral between the two open-shell orbitals responsible for the isoconfigurational S and T states, and is typically ~1 eV for conventional condensed polycyclic aromatic compounds, such as anthracene (4). Because the HSO of aromatic compounds is also small, RISC is generally negligible. However, when the ΔE_ST approaches the thermal energy (~26 meV at room temperature), RISC is induced via thermal excitation, and delayed fluorescence (DF) is subsequently emitted from S1. This is so-called thermally activated DF (TADF), and recent extensive studies on TADF-OLEDs have revealed ηint values of nearly 100% (5–11). According to the semiclassical model of TADF, the rate constant for RISC (kRISC) is given by kRISC ~ A × exp(–ΔE_ST/kBT), where A is the A-exponential factor including HSO, kT is the Boltzmann constant, and T is the temperature (12). Therefore, a high kRISC can be achieved by decreasing ΔE_ST. However, although this idea has been supported by many experimental results, as shown in Fig. 1B (5, 13–19), several papers report fairly high kRISC values even for large ΔE_ST of a few hundred millielectron volts (6, 20). For instance, carbazol-benzonitrile (CzBN) derivatives synthesized by Zhang et al. (20, 21) were reported to have a ΔE_ST of ~0.2 eV. Although the ΔE_ST is too large for efficient RISC at room temperature, CzBN-based OLEDs showed high external EL quantum efficiencies (ηEQE) of ~20%. This ηEQE value means that, under an assumption of a light outcoupling efficiency of OLEDs (22), all the excitons generated electrically were used for EL. A number of fundamental studies using transient PL (TR-PL) spectroscopy and theoretical calculations have been devoted to understand the mechanism of efficient RISC upon a large ΔE_ST of several hundred millielectron volts (6, 23–27). In particular, Dias et al. (25) and Gibson et al. (27) have proposed that the second-order SOC involving the locally excited T state (4LE) and charge-transfer (CT) excited T state (4CT) in thermal equilibrium is crucial for efficient RISC. In the scenario, the spin–allowed transition of 4LE to 4CT excited S state (4CT) in materials having a large ΔE_ST is facilitated efficiently by the vibronic coupling between the 4LE and 4CT states (25, 27). This suggests that RISC is a dynamical process in an excited state. However, this study has been thoroughly conducted for only a few molecules, which consist of a near-orthogonal electron donor (D) and acceptor (A) units. Still, a deeper understanding of the mechanism leading to

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efficient RISC based on a direct observation of excited states formed in both the S and T states is needed to clarify the relationship to the chemical structure and will provide a strategy for the advanced molecular design of TADF molecules.

Here, we used a comprehensive set of complementary experimental techniques, with an emphasis on transient absorption spectroscopy (TAS), to demonstrate that $k_{\text{RISC}}$ cannot be determined by the $D_{\text{ST}}$ alone and strongly relies on the excited states. To understand the mechanism, we focused on Cz-phthalonitrile (CzPN) (5) and CzBN (20, 21) derivatives: 4CzIPN, 2CzPN, 2CzBN, $\alpha$-3CzBN, $m$-3CzBN, $p$-3CzBN, 4CzBN, and 5CzBN (Fig. 1C). Unlike the CzPN derivatives reported previously by our group (5, 19), CzBN derivatives have similar $\Delta E_{\text{ST}}$ values (~0.2 ± 0.04 eV) (see Table 1). In this sense, similar $k_{\text{RISC}}$ values might be expected for CzBN derivatives, but the result is completely different. By looking at excited-state dynamics using TAS, we are able to attribute the different $k_{\text{RISC}}$ to the formation of delocalized excited states, which facilitates RISC. We also identify that a linearly positioned Cz pair in a D-A-D structure (Fig. 1D) is the structural requirement for the formation of delocalized excited state. Our findings provide an advanced general design for TADF molecules with high $k_{\text{RISC}}$ and facilitate the deeper understanding of significant spin up-conversion processes (2).

**RESULTS**

Before examining the excited-state dynamics, we evaluated the fundamental photophysical properties of the CzBN derivatives (Table 1). TR-PL profiles of the CzBN derivatives in oxygen-free toluene show strong DF for 4CzBN and 5CzBN and weak DF for $p$-3CzBN, but no DF for 2CzBN, $\alpha$-3CzBN, or $m$-3CzBN (Fig. 2A). The observed DF...
completely vanished in the presence of oxygen, indicating that the DF is emitted via T states. In Table 1, the $k_{\text{ISC}}$ values of 4CzBN (1.8 \times 10^{-5} \text{ s}^{-1}) and 5CzBN (2.4 \times 10^{-5} \text{ s}^{-1}) are larger than the $k_{\text{ISC}}$ value of p-3CzBN (0.12 \times 10^{-5} \text{ s}^{-1}) by one order of magnitude despite similar $\Delta E_{\text{ST}}$ values of ~0.20 eV for the three materials (Fig. 2B). Moreover, although the $\Delta E_{\text{ST}}$ of o-3CzBN is almost the same as that of 4CzBN, o-3CzBN showed no appreciable DF, that is, $k_{\text{DF}}$ ~ 0 s^{-1}. The rate constants for nonradiative decay of the triplet states ($k_{\text{DF}}$), a competing parameter of $k_{\text{ISC}}$, are of the same order of magnitude for the three 3CzBN isomers at $k_{\text{DF}}$ ~ 10^{-4} \text{ s}^{-1}, although their $k_{\text{ISC}}$ values differ by four orders of magnitude (Table 1). This result indicates that the TADF is activated by the large $k_{\text{ISC}}$ and not because of the suppression of the nonradiative decay path of the triplet states.

When doped at a concentration of 15 weight % (wt %) in a 2,8-bis(diphenylphosphoryl)dibenzo[cd]thiophene (PPT) matrix, 5CzBN showed a PLQY of 78 ± 2%, and OLEDs using 5CzBN reached an EQE of ~4.5%. As judged from the time constant of the prompt fluorescence ($\tau_{\text{prompt}}$) determined by TR-PL (Fig. 3C), we found that the spectral shape for $\Delta \tau > \tau_{\text{prompt}}$ stays unchanged for each molecule because of the almost identical decay lifetimes of T features (Fig. S1). This result indicates that the observed T states are mutually coupled in thermal equilibrium, and facilitate the RISC as a unit for the dynamics of RISC. Therefore, in the following experiments, we focused on the assignment of the excited states of the S and T states (Fig. 3A).

In the time range of $\Delta \tau = 3$ ps, an intense feature at 860 nm with a small shoulder (760 nm), which greatly resembles features commonly observed for cationic mono-Cz (Cz+) compounds (31, 32), was observed for both molecules. Considering that the absorption spectra of 4CzIPN and 2CzPN showed CT characters (5), we assigned the characteristic features at $\Delta \tau = 3$ ps to the absorption of Cz+ moieties (Cz+) formed in the S state by the photoinduced intramolecular CT transitions (figs. S2 and S3). At the same $\Delta \tau$, we found another band in the near-infrared region of 4CzIPN. This band is a so-called charge resonance (CR) band (31) or an inter-valence CT band (32), and it in-
with other rising features at 680 and 1070 nm. These rising features were also observed for 2CzPN in the time range of $\Delta t = 30 \mu$s, but the CR band was not detected. These results indicate that, in the S1 and T1 states, 2CzPN forms a localized CT (loCT) state, whereas 4CzIPN forms both deCT and loCT states in thermal equilibrium. The formation of this delocalized excited T state is consistent with the excited-state scheme for 4CzIPN obtained by time-resolved electron paramagnetic resonance conducted at 77 K (33).

Figure 4A shows contour maps for the TAS results of all six CzBN derivatives in toluene. The TAS spectra at $\Delta t$ in the vicinity of prompt of all the derivatives are depicted in fig. S4. In Fig. 4A, 2CzBN shows an absorption band at around 815 nm, which is assigned to 1Cz$^+$ and thus lo,1CT. After transition through ISC, we found only one T absorption band at around 600 nm. Because the phosphorescence spectrum of 2CzBN (Fig. 2B), with clear vibronic progressions and a long triplet lifetime of $\sim 5$ s, was in good agreement with that of tricarbazolyl benzene (TCzB; inset in Fig. 2B), the T1 state of 2CzBN is considered to be the same as that of TCzB and, thereby, is assigned to a localized state on a mono-Cz moiety with pure $p$-$p^*$ character (34). In this context, the T1 absorption band at around 600 nm can be ascribed to the $p$-$p^*$ transition of a neutral mono-Cz state (3LE).

Similar to 2CzBN, the TAS spectra of o-3CzBN show a 1Cz$^+$ band at around 850 nm before ISC and a 3LE band at around 600 nm after ISC. In addition, o-3CzBN exhibited another T band at around 1150 nm. Because the T1 character of o-3CzBN is understood as a mixing of the CT and LE states based on the vibronic-less phosphorescence spectrum (Fig. 2B) with a short lifetime ($\sim 1$ s) (34), the feature at around 1150 nm can be attributed to the absorption of the loCT state of 3Cz$^+$ (lo,3CT). These spectral characteristics are also observed for m-3CzBN, implying the formation of the same excited states.

Finally, we look at the dynamics of TADF-active CzBN derivatives. Clear 1Cz$^+$ and 3Cz$^+$ bands were observed in addition to 1Cz$^+$, 3LE, and 3Cz$^+$ bands for 5CzBN, similar to 4CzIPN, indicating the formation of lo,1CT and de,1CT in the S1 state and 3LE, lo,3CT, and de,3CT in
the T₁ state, respectively. On the other hand, for 4CzBN, ¹Cz⁺ and ³Cz₂⁺ bands were observed in the S₁ state, but no ³Cz⁺ band was seen after relaxation via ISC and only ³LE and strong ³Cz₂⁺ bands were formed (see also Fig. 4B). The phosphorescence spectra of 4CzBN and p-3CzBN show rather vibronic-less features resembling their fluorescence spectra (see Fig. 2B), indicating a strong CT character in the T₁ state (34) because of the formation of deCT state. For p-3CzBN, the TAS spectra were essentially the same as those of 4CzBN, except for the energy positions, suggesting a similar T₁ character and RISC process as for 4CzBN.

The formation of the deCT state is also reflected in the electronic structure of the CzBN derivatives. In the ground-state absorption spectra (Fig. 4C) of p-3CzBN, 4CzBN, and 5CzBN, a characteristic CT band is observed as the lowest energy transition (CT₁), which differs from the commonly observed CT band (CT₁) and π-π* band of Cz moieties. Furthermore, CT₁ forms all for the CzBN derivatives, except p-3CzBN and 4CzBN. From these results, we can assign CT₁ and CT₂ to originate from the formation of loCT and deCT characters, respectively. This assignment is consistent with the TAS results, which suggest that p-3CzBN, 4CzBN, and 5CzBN form a deCT state in the S₁ state, whereas other CzBN derivatives exhibit a loCT state. The same consideration is applicable to 4CzIPN and 2CzPN (Fig. 3B and fig. S2).

**DISCUSSION**

The combined results of all structural, photophysical, excited-state, and OLED studies provide a comprehensive answer to the question of why kₕRISC of the CzBN derivatives does not necessarily depend on ΔErot. Molecules exhibiting TADF showed deCT states (that is, ¹Cz₂⁺ and ³Cz₂⁺) and a ³LE state, whereas TADF-inactive molecules exhibited only a ³LE state or a combination of ³LE state and loCT states (that is, ¹Cz⁺ and ³Cz⁺). This indicates, for CzBN derivatives, that neither the presence of only a ³LE state nor a combination of ³LE and deCT states is a sufficient condition for the activation of TADF, and instead, the presence of a deCT state is the key factor for increasing kₕRISC. The deCT facilitates RISC irrespective of ΔErot. However, this does not exclude the contribution of the combination of loCT and ³LE states to kₕRISC as 2CzPN, which showed these two states (Fig. 3B) has been reported to exhibit weak TADF (4.2 percentage point contribution to a total PLQY of 46%) (18). This result suggests that a combination of loCT and ³LE states can also be essentially involved in the RISC process if a D unit is combined with a strong A unit, such as PN. That is, the stabilization of the CT state is an important factor for enhancing kₕRISC.

Now, the practically relevant question is what are the structural requirements for deCT formation? The TAS results of the CzBN derivatives demonstrated that the position of the Cz units connected to the BN core is important. Namely, the positioning of Cz moieties at 2 and 3 (2CzBN) or 2, 4, and 6 (m-3CzBN) cannot satisfy the structural requirement (see Fig. 1C). Although the Cz at the 4-position of o-3CzBN might be expected to tend to form Cz⁺ because of the low electron density, the TAS results showed that the Cz at the 4-position does not form a CR band with the neighboring Cz moieties at the 3- or 5-position. In addition, we confirmed that the Cz at the 2-position does not play a role in the CR band of p-3CzBN because movement of the Cz from 2- to 4-position in p-3CzBN also showed the CR band (fig. S5). Consequently, we identify the common structure among the
TADF-active molecules as a pair of Cz units connected linearly with a bridging A unit, that is, at 2- and 5-positions or 3- and 6-positions (Fig. 1D). This structural scheme is regarded as a linear D-A-D structure, and the linearly positioned Cz pair in the D-A-D structure is identified as the origin of the deCT states. Notably, a D-A-D structure has been a common chemical template of TADF molecules, but the linear D-A-D structure proposed here is a new connection rule for the D and A moieties within a category of D-A-D structures. Furthermore, the linear D-A-D structure is extremely simple, and a combination of other kinds of D and A units may facilitate RISC by forming deCT states.

We next discuss a mechanism leading to high $k_{\text{RISC}}$ via deCT in terms of excited-state dynamics. Generally, RISC is intrinsically forbidden between $^3\text{CT}$ and $^1\text{CT}$ states because of a vanishing of the SOC matrix elements between their molecular orbitals and it is facilitated by SOC between $^3\text{LE}$ and $^1\text{CT}$ (25, 27). In addition, as Gibson et al. (27) demonstrated theoretically, a vibronic coupling between the $^3\text{CT}$ and $^3\text{LE}$ states plays a crucial role in the production of $^1\text{CT}$ states via RISC. In this context, the energy gap to overcome for RISC is not $\Delta E_{\text{ST}}$ but the energy difference between $^3\text{LE}$ and $^1\text{CT}$, as here defined to $\Delta E_{\text{ST(LE)}}$, and a mutual coupling among the T states in thermal equilibrium is the key for efficient RISC.
vibronic coupling can occur between the 3LE and 3CT, but the coexistence of photochemistry and the development of high-performance OLEDs, as well as future molecular light-emitting devices.

Finally, we propose a comprehensive design strategy for TADF molecules to obtain a high PLQY. Although 4CzBN and 5CzBN exhibit comparable PLQY values (~0.2 eV), the ΔE_{ST(LE)} values of the TADF-active molecules are similar to their ΔE_{ST} values (~0.2 eV), the ΔE_{ST(LE)} values of the TADF-active molecules are 0.12, 0.01, and ~0.06 eV for p-3CzBN, 4CzBN, and 5CzBN, respectively, which are all smaller than their corresponding ΔE_{ST} values. This result is caused by the lowering of the S1 state for 3CT while suppressing the structural relaxation by introducing bulky moieties around linearly positioned D units in a D-A-D structure. The simple design strategy established here will be extremely beneficial for the design of new TADF molecules, and we believe that our work contributes to the progression of photochemistry and the development of high-performance OLEDs, as well as future molecular light-emitting devices.

MATERIALS AND METHODS

Materials

4CzIPN, 2CzPN, m-3CzBN, 4CzBN, and 5CzBN were synthesized according to literature procedures (5, 20, 21). 2CzBN, o-3CzBN, and p-3CzBN were newly synthesized. The synthetic procedures and characterization are described in the Supplementary Materials. All the materials were purified by thermal sublimation. Solutions were prepared by dissolving the purified molecules in toluene (purity, 99.8%). The solution concentration was 10⁻³ to 10⁻⁵ M, depending on the samples and measurements.

Optical characterization of TADF molecules

The solutions were characterized by measuring the steady-state ultraviolet-visible (UV-VIS) absorption/PL spectra and TR-PL. TR-PL was measured using a C11367-01 spectrometer (Hamamatsu Photonics) or a Fluorocube fluorescence lifetime system (HORIBA). The PLQY of the solutions was measured by an absolute PLQY measurement system (C11347-01, Hamamatsu Photonics), with an excitation wavelength of 337 nm. Before the TAS and TR-PL measurements, the solutions were deoxygenated with dry nitrogen gas to eliminate the deactivation of triplets. The effect of deoxygenation was confirmed by comparing τ_{prompt} and τ_{TADD} values with those reported by Uoyama et al. (5).

OLED fabrication and characterization

Glass substrates with a prepatterned, 100-nm-thick, 100 ohm/square tin-doped indium oxide (ITO) coating were used as anodes. After pre-cleaning of the substrates, effective device areas of 4 mm² were defined by the patterned ITO substrates by a polyimide insulation layer using a conventional photolithography technique. Organic layers were formed by thermal evaporation. Doped emitting layers were deposited by coevaporation. Deposition was performed under vacuum at pressures <5 × 10⁻⁵ Pa. After device fabrication, devices were immediately encapsulated with glass lids using epoxy glue in a nitrogen-filled glove box [O₂ < 0.1 parts per million (ppm) and H₂O < 0.1 ppm]. OLEDs with the structure ITO/4,4'-N,N'-bis(4-methylphenyl)benzeneamine] (TAPC) (35 nm)/mCP (10 nm)/dopant (15 wt %);PPT (30 nm)/PPT (40 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated. The current density–voltage–luminance characteristics of the OLEDs were evaluated using a source measurement meter (B2912A, Agilent) and a calibrated spectroradiometer (CS-2000A, Konica Minolta Sensing Inc.). EL spectra were collected using a spectroradiometer (simultaneously with luminance). The η_{EQE} was calculated from the front luminance, current density, and EL spectrum. All measurements were performed under an ambient atmosphere at room temperature.

Figure 4D shows ΔE_{ST(LE)} and ΔE_{ST} of all the CzBN derivatives, which are taken from Fig. 2B. Here, the 3LE level observed only for 2CzBN is used as a common one for all the CzBN derivatives because the 3LE, which originates from a phenyl-Cz, is not significantly affected by adding acceptor substituents (see the phosphorescence spectrum of 2CzBN and TCBz in Fig. 2B). It is seen that, although the ΔE_{ST(LE)} values of the TADF-inactive molecules are similar to their ΔE_{ST} values (~0.2 eV), the ΔE_{ST(LE)} values of the TADF-active molecules are 0.12, 0.01, and ~0.06 eV for p-3CzBN, 4CzBN, and 5CzBN, respectively, which are all smaller than their corresponding ΔE_{ST} values. This result is caused by the lowering of the S1 state for 3CT while suppressing the structural relaxation by introducing bulky moieties around linearly positioned D units in a D-A-D structure. The simple design strategy established here will be extremely beneficial for the design of new TADF molecules, and we believe that our work contributes to the progression of photochemistry and the development of high-performance OLEDs, as well as future molecular light-emitting devices.
For femtosecond-TAS, we used the third harmonic of the fundamental beam (800 nm) generated by a β-barium borate crystal, whereas the white-light continuum generated by focusing the fundamental beam (800 nm) onto a sapphire plate (2 mm thick) was used as the probe light. For nanosecond-TAS, we used the third harmonic of fundamental light (800 nm) generated by a Nd:YAG laser (wavelength, 355 nm; FWHM pulse, <150 ps; repetition, 10 Hz) as the pump light and a xenon flash lamp as the probe light. The system of nanosecond-TAS was used for microsecond-TAS measurements, but the probe light was exchanged with a xenon steady-state lamp. Although the strong intensity of the flash lamp was suitable for measurements with a fast response time (~1 ns), the use of the steady lamp could cover Δt ~ 100 ms with a slow response time of 10 to 30 ns. The irradiated intensity of the pump laser was set to 0.21 and 0.27 mJ/cm² for femtosecond-TAS measurements of 4CzPN and 2CzPN, respectively, and 0.7 to 1.4 mJ/cm² for nanosecond- and microsecond-TAS measurements of all the derivatives. After the TAS measurements, UV-VIS absorption spectra were measured to check the sample degradation by laser irradiation. We noted that the long-duration irradiation of the femtosecond-pulse laser gave rise to a decrease of a first CT band (CT2) in the UV-VIS absorption spectra, in particular for 4CzIPN (fig. S2). Therefore, we carefully conducted the TAS measurements by checking the data reproducibility. All measurements were carried out at 295 K. In Fig. 3A, ΔOD of the microsecond-TAS spectra at Δt = 4.6 and 30 μs was corrected with reference to the intensity of nanosecond-TAS at Δt = 27 ns; the ΔOD of the nanosecond-TAS was also corrected in advance using femtosecond-TAS at Δt = 2 ns. The linearity of ΔOD for each correcting process was guaranteed by considering the time resolution of microsecond- and nanosecond-TAS measurements.

Supplementary Material
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/5/e1603282/DC1

Synthesis and characterization of 2CzBN, α-3CzBN, and p-CzBN
Fig. S1. Time profiles of TAS of various triplet states of 4CzIPN and 2CzPN in toluene. Fig. S2. Steady-state absorption spectra. Fig. S3. Laser power dependence in TAS spectra. Fig. S4. TAS spectra of the CzBN derivatives. Fig. S5. TAS results of 3, 4, 6-p-CzBN. Fig. S6. Energy position of CR band. Fig. S7. Emission spectra of CzPN derivatives. Fig. S8. Time profiles of TAS of triplet states of CzBN derivatives.

References and Notes


Acknowledgments: We thank W. J. Potscavage Jr. for assistance with the preparation of this manuscript and T. Yoshioka for assistance with this project. Funding: This work was supported, in part, by the “Development of Fundamental Evaluation Technology for Next-Generation Chemical Materials” program commissioned by the New Energy and Industrial Technology Development Organization, and the International Institute for Carbon Neutral Energy Research (I2CNER) sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Author contributions: T.H. and H.M. performed TAS measurements and T.H., H.M., A.F., and H. Nakanotani analyzed the data. T.H. and H. Nakanotani determined photophysical properties and analyzed the data. K.N. and H. Nomura prepared CzPN and CzBN derivatives. H. Nakanotani fabricated OLEDs and analyzed the data. T.H. and H. Nakanotani coordinated the work and wrote the paper. K.T., T.T., M.Y., and C.A. conceived the project, and all authors critically commented on the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 26 December 2016
Accepted 9 March 2017
Published 10 May 2017
10.1126/sciadv.1603282

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Sci Adv 3 (5), e1603282.
DOI: 10.1126/sciadv.1603282