Thermal equilibration between singlet and triplet excited states in organic fluorophore for submicrosecond delayed fluorescence

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In any complex molecular system, electronic excited states with different spin multiplicities can be described via a simple statistical thermodynamic formalism if the states are in thermal equilibrium. However, this ideal situation has hitherto been infeasible for efficient fluorescent organic molecules. Here, we report a highly emissive metal-free purely organic fluorophore that enables thermal equilibration between singlet and triplet excited states. The key to this unconventional excitonic behavior is the exceptionally fast spin-flipping reverse intersystem crossing from the triplet to singlet excited states with a rate constant exceeding $10^{6}$ s$^{-1}$, which is considerably higher than that of radiative decay (fluorescence) from the singlet excited state. The present fluorophoric system exhibits an emission lifetime as short as 750 nanoseconds and, therefore, allows organic light-emitting diodes to demonstrate external electroluminescence quantum efficiency exceeding 20% even at a practical high luminance of more than 10,000 candelas per square meter.

**INTRODUCTION**

The spin dynamics of excited-state molecules play a pivotal role in organic optoelectronic devices. In organic light-emitting diodes (OLEDs), the population of spin-singlet and spin-triplet excited states determines the internal electroluminescence (EL) quantum efficiency ($\eta_{\text{EL}}$). Over the past two decades, two different classes of luminescent materials have been established for the harvesting of triplet excitons to achieve light emission at $\eta_{\text{EL}}$ values that approach 100% in OLEDs. The first involves organometallic complexes containing precious metals, such as iridium and platinum, to induce strong spin-orbit coupling (SOC), thereby allowing triplet excitons to emit light as phosphorescence (1–4). The second class of materials is based on purely organic molecules that exhibit thermally activated delayed fluorescence (TADF) (5–14). The latter class of molecules has energetically close lowest-energy singlet ($S_1$) and triplet ($T_1$) excited states, where thermal energy at room temperature promotes an up-conversion of dark $T_1$ excitons into radiative $S_1$ excitons via reverse intersystem crossing (RISC), resulting in temporally delayed fluorescence. Although certain organic molecules emit TADF without precious metals, the relatively long-lived $T_1$ excitons cause a severe efficiency roll-off in OLEDs in high-luminance operations owing to bimolecular recombination such as triplet-triplet annihilation (15–17).

In modeling the kinetics of TADF, the $S_1$ and $T_1$ states are often approximated to be in thermal equilibrium (Fig. 1). This approximation may work well in classical less-emissive TADF molecules, such as fullerenes (18), with long excited-state lifetimes of over tens of milliseconds. However, highly luminescent modern TADF emitters used in OLEDs exhibit fast radiative decay from the $S_1$ state to the ground ($S_0$) state with rate constants ($k_r$) exceeding $10^{6}$ s$^{-1}$, which are generally much higher than the rate constants of RISC from $T_1$ to $S_1$ (5–14). Consequently, the slowest RISC becomes the rate-limiting process in TADF, and thermal equilibrium approximation cannot be applied. Unlocking this rate limitation in TADF stemming from slow RISC is highly desirable for the realization of efficient short-lived emissions from equilibrated excited states and, consequently, minimization of the intrinsic efficiency roll-off in TADF-OLEDs.

Here, we demonstrate that a metal-free purely organic fluorophore based on thioxanthone (TXT) can allow exceptionally fast RISC and intersystem crossing (ISC) with rate constants ($k_{\text{RISC}}$ and $k_{\text{ISC}}$) both exceeding $10^{8}$ s$^{-1}$ at 300 K, thereby enabling quasi-static equilibrium between the $S_1$ and $T_1$ states. This can be realized without impairing the high luminescence efficiency of the fluorophore. The temperature dependence of its submicrosecond-order delayed fluorescence can be rationalized by a simple ideal kinetic model that assumes equilibrium between the $S_1$ and $T_1$ states (Fig. 1). By virtue of the excited-state equilibrium and short submicrosecond emission lifetime, TADF-OLEDs using this TXT-cored fluorophore achieved remarkable suppression of the efficiency roll-off, with an external EL quantum efficiency ($\eta_{\text{ext}}$) exceeding 20%, even at a practical high luminance of 10,000 cd m$^{-2}$. This study provides an advanced and promising concept for truly efficient exciton harvesting beyond the framework of conventional time-delaying TADF limited by slow RISC.

**Fig. 1. Fluorescence from equilibrated excited states.** Simplified electron spin configurations representing fluorescence from thermally equilibrated $S_1$ and $T_1$ states. Unlike conventional TADF systems, this equilibrium model is valid only when both $k_{\text{ISC}}$ and $k_{\text{RISC}}$ are significantly higher than $k_r$. 

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RESULTS

Fluorophore design
In the fundamental physical mechanism of RISC, a strong SOC can allow the intrinsically spin-forbidden transition from $T_1$ to $S_1$ states and thereby enhance $k_{\text{RISC}}$. Actual TADF emitters based on electronic donor-acceptor $\pi$-systems involve energetically close-lying complex excited states comprising the singlet and triplet intramolecular charge-transfer states (denoted by $1\text{CT}$ and $3\text{CT}$) and the triplet locally excited state ($3\text{LE}$). Prior theoretical studies have suggested that the SOC between $1\text{CT}$ and $3\text{CT}$ is too weak to account for the experimentally observed $k_{\text{RISC}}$ of $10^4$ to $10^6$ s$^{-1}$ in common TADF emitters. This requires us to consider the involvement of $3\text{LE}$ as an intermediate excited state in RISC, which can provide an effective SOC between the $1\text{CT}$ and $3\text{LE}$ states with different orbital symmetries necessary for spin flipping in accordance with the El-Sayed rule \cite{19–25}. Very recently, we revealed that in heteraborin-based TADF emitters, the incorporation of a heavier sulfur atom instead of oxygen and nitrogen lead to an intensified SOC between the $1\text{CT}$ and $3\text{LE}$ states and, thus, a remarkably high $k_{\text{RISC}}$ approaching $10^7$ s$^{-1}$, which is comparable to $k_r$ \cite{26–28}. The introduction of heteroatoms with lone-pair electrons or empty orbitals results in an effective perturbation to the excited-state electronic configurations for accelerating RISC. Hence, we designed and synthesized a new donor-acceptor fluorophore, MCz-TXT (Fig. 2A), that features sulfur-containing TXT as an acceptor core coupled with two 1,3,6,8-tetramethylcarbazole (MCz) donor units. For comparison, its oxygen analog, MCz-XT with a xanthone (XT) \cite{29, 30} acceptor core, was also developed. MCz-TXT and MCz-XT were synthesized via the palladium-catalyzed Buchwald-Hartwig amination of 3,6-dibromothioxanthone and 3,6-dibromoxanthone, respectively, with two equivalents of MCz. The detailed synthesis procedures and characterization data are provided in the Supplementary Materials.

Photophysical properties
The photophysical properties of MCz-TXT and MCz-XT were analyzed as dilute solutions in toluene and as doped thin films in host matrices of 3,3’-bis(carbazol-9-yl)biphenyl (mCBP) (Fig. 2B). Both molecules had nearly identical optical bandgaps of 2.8 eV, as estimated from the intersection points of the normalized absorption and emission spectra of their $1\text{CT}$ transition bands. Upon photoexcitation, the deoxygenated MCz-XT solution displayed fluorescence with an emission peak ($\lambda_{\text{PL}}$) at 500 nm and an absolute photoluminescence (PL) quantum yield ($\Phi_{\text{PL}}$) of 84%, whereas the MCz-TXT solution exhibited a slightly red-shifted $\lambda_{\text{PL}}$ at 508 nm with $\Phi_{\text{PL}}$ of 79%. In the doped films, both MCz-TXT and MCz-XT showed intense sky-blue fluorescence ($\lambda_{\text{PL}} = 490$ and 482 nm, respectively), and their $\Phi_{\text{PL}}$ values increased to 92 and 95%, respectively, in a nitrogen atmosphere (Fig. 2C). However, under aerated atmospheric conditions, the $\Phi_{\text{PL}}$ values of the MCz-TXT and MCz-XT doped films decreased to 55 and 70%, respectively, due to the quenching of the triplet excitons by molecular oxygen.

Fig. 2. Molecular structures and photophysical properties. (A) Molecular structures of MCz-TXT and MCz-XT. (B) Steady-state absorption and photoluminescence (PL) spectra of MCz-TXT and MCz-XT in toluene ($1.0 \times 10^{-5}$ M), a.u., arbitrary units. (C) Steady-state PL spectra of their 10 wt % (weight %) doped films in 3,3’-bis(carbazol-9-yl) biphenyl (mCBP) host matrices. (D and E) Transient PL decay profiles of the doped films of MCz-TXT (D) and MCz-XT (E) measured at varying temperatures. (F) Temperature dependence of the delayed fluorescence rate constants ($k_{\text{DF}}$) in the doped films. The solid lines in (F) represent theoretically predicted values using the equilibrium model described by Eq. 1, where the experimentally determined radiative decay rate constants ($k_r = 1.3 \times 10^7$ and 2.0 $\times 10^7$ s$^{-1}$) and energy gaps between the $S_1$ and $T_1$ states ($\Delta E_{ST} = 30$ and 10 meV for MCz-TXT and MCz-XT, respectively) are adopted for simulations.
To unveil the excited-state kinetics of MCz-TXT and MCz-XT, we performed transient PL decay measurements on the doped films at varying temperatures (Fig. 2, D and E). Both fluorophores showed the distinct biexponential PL decay characteristics of TADF consisting of a nanosecond-order prompt fluorescence, followed by delayed fluorescence with temperature-dependent emission lifetimes. The delayed fluorescence lifetimes (τDF) of MCz-TXT and MCz-XT were as short as 750 and 940 ns, respectively, at 300 K. In comparison, much longer emission lifetimes were observed for a representative TADF emitter, 2,4,5,6-tetra(carbazol-9-yl)isophthalonitrile (4CzIPN) (7) (τDF = 2.8 μs; Fig. S1A), and even for an iridium-based phosphorescent emitter, bis[4,6-difluorophenyl]pyridinato(picolinato) iridium(III) (FIrpic) (31) (τphos = 1.7 μs; Fig. S1B), in the same host matrices. Furthermore, it was found that the temperature-dependent delayed fluorescence behavior of MCz-TXT follows a kinetic model assuming thermal equilibration between the S1 and T1 states (Fig. 2F, red line), as expressed below

$$k_{DF} = \frac{1}{3} k_e \exp \left( \frac{-\Delta E_{ST}}{k_B T} \right)$$

(1)

where $k_{DF} (= \tau_{DF}^{-1})$ is the delayed fluorescence rate constant, $\Delta E_{ST}$ is the energy gap between the S1 and T1 states, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. A scaling factor of $1/3$ is designated to account for the spin multiplicity of the S1 and T1 states (32). For MCz-TXT, the best-fit parameters of the experimental temperature dependence of $k_{DF}$ to Eq. 1 were calculated to be $k_e = 1.5 \times 10^{10} \text{ s}^{-1}$ and $\Delta E_{ST} = 35 \text{ meV}$.

These values are consistent with the $k_e$ value of $1.3 \times 10^{10} \text{ s}^{-1}$ independently determined from the prompt fluorescent decay profile (Fig. S2) and the $\Delta E_{ST}$ value of 30 meV derived from the low-temperature fluorescence and phosphorescence spectra (Fig. S3). This result unambiguously proves the validity of the equilibrium model for describing the excited-state kinetics of MCz-TXT demonstrated in this study. Note that quasi-static equilibration between the S1 and T1 states is attainable even in such a highly emissive purely organic fluorophore. In contrast, for MCz-XT, the equilibrium model (Fig. 2F, blue line) overestimates the $k_{DF}$ values by a factor of 3 to 4 compared to the corresponding experimental values due to the slower RISC in MCz-XT, similar to the cases of conventional TADF emitters including 4CzIPN (Fig. S4).

Further kinetic analysis of the transient PL characteristics revealed that MCz-TXT has an unexpectedly high $k_{RISC}$ of $1.1 \times 10^{9} \text{ s}^{-1}$ and, likewise, a high $k_{ISC}$ of $9.4 \times 10^{6} \text{ s}^{-1}$ at 300 K (Table 1). These rate constants are substantially higher than the measured $k_e$ of $1.3 \times 10^{10} \text{ s}^{-1}$, as indicated by the equilibrium model, and are almost two orders of magnitude higher than those measured for MCz-XT ($k_{RISC} = 2.7 \times 10^{8} \text{ s}^{-1}$ and $k_{ISC} = 3.4 \times 10^{9} \text{ s}^{-1}$) and 4CzIPN ($k_{RISC} = 1.9 \times 10^{8} \text{ s}^{-1}$ and $k_{ISC} = 7.7 \times 10^{8} \text{ s}^{-1}$). The marked differences in $k_{RISC}$ and $k_{ISC}$ between MCz-TXT and MCz-XT can be explained by an exciton transformation model assuming that RISC and ISC are dependent on the SOC and occur at the crossing point between the potential energy surfaces of the singlet and triplet excited states (Fig. 3A). At the crossing point, the energies of the two different spin states are regarded to be identical, as driven by the thermal energy $k_B T$ (approximately 25.8 meV at 300 K). Thus, $k_{RISC}$ and $k_{ISC}$ are described by the rate expressions of the Marcus theory (33, 34)

$$k_{RISC} = \frac{2\pi}{h} H_{SO}^2 \left( 4\pi \lambda_{RISC} k_B T \right)^{-1/2} \exp \left( \frac{-E_{a,RISC}}{k_B T} \right)$$

(2)

where $H_{SO}$ is the SOC strength between the associated singlet and triplet excited states, $\lambda$ is the reorganization energy, and $E_a$ is the activation energy. Evidently, $H_{SO}$ scales $k_{RISC}$ and $k_{ISC}$ equally, whereas the path-dependent $\lambda$ and $E_a$ primarily lead to the discrepancy between $k_{RISC}$ and $k_{ISC}$. As shown in Fig. 3 (B and C), Eqs. 2 and 3 well reproduce the experimental temperature dependence of $k_{RISC}$ and $k_{ISC}$ for MCz-TXT with the $H_{SO}$ of 0.37 meV (Table 1), which is more than one order of magnitude larger than those of MCz-XT ($H_{SO} = 0.020 \text{ meV}$) and 4CzIPN ($H_{SO} = 0.035 \text{ meV}$). According to Eqs. 2 and 3, the faster RISC of MCz-TXT (with $k_{RISC}$ of $1.1 \times 10^{9} \text{ s}^{-1}$) is primarily attributable to its larger $H_{SO}$, although MCz-TXT contains no heavy metal elements. Although sulfur, a typical third-row element, is not generally regarded as a heavy atom, we ascertained that merely replacing an oxygen atom in XT by a sulfur atom in TXT markedly enhanced the SOC, thereby accelerating the RISC and shortening the resultant emission lifetime.

**Computational simulations**

To further elucidate the origin of the large $H_{SO}$ affording the fast RISC/ISC in MCz-TXT, we performed time-dependent density functional theory (TDDFT) calculations using the Breit-Pauli spin-orbit Hamiltonian (35) and simulated the lowest-energy singlet-triplet crossing point (36). For all three molecules, the calculated values of $\lambda$, $E_a$, and $H_{SO}$ based on the RISC/ISC models agreed reasonably with the experimental results (Table 1). Consequently, their theoretical $k_{RISC}$ values were calculated to be within the same order of magnitude as the corresponding experimental values using Eq. 3. The lowest-energy crossing points were eventually found to be between S1 and T2 rather than between S1 and T1. This result can be explained by the same CT electronic configurations of the S1 and T1 excitations, which are unable to energetically cross along with the molecular geometry changes. As presented in Fig. 3D, the natural transition orbital analysis of MCz-TXT demonstrates the same CT nature of S1 and T1 whereas its energetically close-lying T2 excitation is dominated by the $\pi-\pi^*$ transition involving a significant contribution from the sulfur atom in the TXT acceptor unit. Such a distinct change in the orbital symmetries between the S1 and T1 states is attainable even in such a highly emissive purely organic fluorophore. In contrast, for MCz-XT, the equilibrium model (Fig. 2F, blue line) overestimates the $k_{DF}$ values by a factor of 3 to 4 compared to the corresponding experimental values due to the slower RISC in MCz-XT, similar to the cases of conventional TADF emitters including 4CzIPN (Fig. S4).

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**OLED performance**

To demonstrate the benefits of the TXT-cored fluorophore capable of forming equilibrated excited states, we fabricated and tested OLEDs using MCz-TXT and MCz-XT in the emission layer (EML). To compare the device performances, we used 4CzIPN and FIrpic as exemplary typical TADF and phosphorescent emitters, respectively. The fabricated OLEDs consist of the following layer sequence

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(Fig. 4A): indium tin oxide (ITO)/2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexaazatriphenylene (HAT-CN; 5 nm)/1,1-bis[4-N,N-di(p-tolyl)amino]phenyl)cyclohexane (TAPC; 40 nm)/9-phenyl-3,9′-bicarbazole (CCP; 10 nm)/10 wt % (weight %) emitter:mCBP (20 nm)/2,8-bis(diphenylphosphinyl) dibenzo[b,d]furan (PPF; 10 nm)/1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (B3PyPB; 60 nm)/8-hydroxyquinolinato lithium (Liq; 1 nm)/Al (100 nm). Figure 4 (B to D) compares the EL spectra, current density–voltage–luminance (J–V–L) characteristics, and ηext characteristics of the fabricated devices, whereas Table 2 compiles their key EL parameters.

The EL spectrum of each of the four devices originated solely from the corresponding emitter without additional emissions from the adjacent layers (Fig. 4B), indicating that the electrogenerated excitons were well confined within the EML. The maximum ηext of the MCz-TXT–based device reached 25.8%, which corresponds to ηint of nearly 100% for a bottom-emission OLED with a typical light-out-coupling efficiency of 20 to 30%. The ηext value remained as high as 21.6% even at a high luminance of 10,000 cd m⁻². Note that the viewing angle dependence of the EL intensities followed a Lambertian distribution (Fig. 4D, inset), which ensures the accuracy of the ηext measured from the forward emission. Although comparably high maximum EL efficiencies were obtained with the other emitters as well, their ηext tended to decline more sharply as the luminance increased (ηext = 19.7% for MCzXT, 16.7% for 4CzIPN, and 17.5% for Flrpic at 10,000 cd m⁻²). The efficiency roll-offs of these OLEDs were further quantified by the critical current density (J90%), at which ηext dropped to 90% of its maximum value. The MCz-TXT–based device showed a higher J90% of 6.1 mA cm⁻² than

| Emitter | kRISC (s⁻¹) | kISC (s⁻¹) | λRISC (meV) | λISC (meV) | EaRISC (meV) | EaISC (meV) | ηSOC (meV) |
|---------|-------------|-------------|-------------|-------------|--------------|--------------|-------------|
| MCz-TXT | Exp. 1.1 × 10⁸ | 9.4 × 10⁸ | 594 | 175 | 33 | 0.29 |
| Calc. 3.4 × 10⁹ | 1.5 × 10⁹ | 50 | 340 | 120 | 57 | 0.70 |
| MCz-XT | Exp. 2.7 × 10⁹ | 3.4 × 10⁷ | 640 | 13 | 31 | 0.020 |
| Calc. 6.2 × 10⁶ | 2.8 × 10⁷ | 48 | 340 | 95 | 30 | 0.057 |
| 4CzIPN | Exp. 1.9 × 10⁶ | 7.7 × 10⁷ | 89 | 11 | 92 | 25 | 0.035 |
| Calc. 1.1 × 10⁶ | 2.6 × 10⁷ | 26 | 35 | 160 | 80 | 0.074 |

Fig. 3. Excited-state kinetics and electronic configurations. (A) Schematic potential energy surfaces of excited states depicting the nonadiabatic spin-flipping RISC and ISC. (B and C) Temperature dependence of the rate constants of RISC (B) and ISC (C) of MCz-TXT, MCz-XT, and 4CzIPN in 10 wt % emitter:mCBP doped films. The solid lines in (B) and (C) represent the fits to the nonadiabatic RISC and ISC models represented by Eqs. 2 and 3, respectively. (D and E) Natural transition orbitals for the excited states of MCz-TXT (D) and MCz-XT (E) at the lowest-energy crossing points between the potential energy surfaces of the singlet and triplet excited states.
the other devices ($J_{90\%} = 3.6 \text{ mA cm}^{-2}$ for MCz-XT, 3.8 mA cm$^{-2}$ for 4CzIPN, and 5.5 mA cm$^{-2}$ for FIrpic). The minimal efficiency roll-off for the MCz-TXT–based device is mainly ascribed to its shorter emission lifetime, which effectively contributes to alleviation of the triplet exciton accumulation and the suppression of the competing bimolecular recombination in the high current density (or luminance) regime.

### DISCUSSION

We proposed a design strategy to attain singlet-triplet equilibration in purely organic fluorophores for truly efficient exciton transformation. The designed TXT-cored fluorophore, MCz-TXT, exhibited sky-blue TADF emission with an ultrashort delayed fluorescence lifetime of 750 ns and a high PL quantum yield of 92% in solid thin films. The combined experimental and theoretical study revealed that its ideal excitonic characteristics originated from its exceptionally fast RISC and ISC with rate constants of over $10^8 \text{ s}^{-1}$, which are approximately two orders of magnitude higher than those of typical efficient TADF emitters including 4CzIPN. For MCz-TXT, the spin-flipping RISC should no longer be the rate-limiting process over the entire TADF process, as a result of the intensified SOC between the singlet and triplet excited states that arises from the additional perturbation by the strategically introduced sulfur atom.

The sky-blue TADF-OLED based on MCz-TXT achieved a high maximum $\eta_{\text{ext}}$ of 25.7%, which remained as high as 21.6% even at a practical high luminance of 10,000 cd m$^{-2}$, outperforming the sky-blue phosphorescent OLED using FIrpic. On the basis of this novel
design principle for singlet-triplet equilibrium, the further exploration of the vast chemical space promises to produce key technologies that minimize the intrinsic efficiency roll-off and overcome the bottleneck of conventional TADF-OLEDs.

MATERIALS AND METHODS

Materials

The synthetic procedures and characterization data for MCz-TXT and MCz-XT are described in the Supplementary Materials.

Photophysical measurements

Thin-film samples for photophysical measurements were deposited on quartz substrates via vacuum deposition using an E-200 vacuum evaporation system (ALM Technology). The ultraviolet (UV)–visible absorption and PL spectra were measured using a V-670 spectrophotometer (Jasco) and an FP-8600 spectrophotometer (Jasco), respectively. The absolute PL quantum yields (ΦPL) were determined using an IL-835 integrating sphere system (Jasco). Transient PL decay measurements were performed using a C11367 Quantaurus-Tau fluorescence lifetime spectrometer (Hamamatsu Photonics) with a 280-nm LED excitation source under a nitrogen atmosphere.

Quantum chemical calculations

All quantum chemistry calculations were performed using the Gaussian 09 suite of programs. Gas-phase geometry optimizations for the lowest-energy singlet and triplet excited states were performed using TDDFT with the LC-BLYP functional (37) and the 6-31G(d) basis set within the Tamm-Dancoff approximation (38). The separate parameters for the LC-BLYP functional were optimized for each molecule to incorporate a reasonable exchange (39). Geometry optimizations for the lowest-energy crossing points between the potential energy surfaces of the singlet and triplet excited states were performed at the same level of theory, using the gradient projection method implemented in the GRRM14 program (36). SOCs were calculated using the Breit-Pauli Hamiltonian with an effective charge approximation implemented in the PySOC program (35).

Device fabrication and evaluation

Prepatterned ITO-coated glass substrates were cleaned with detergent, deionized water, acetone, and isopropanol. Subsequently, the substrates were subjected to UV-ozone treatment for 30 min before being loaded into an E-200 vacuum evaporation system (ALM Technology). Organic layers and an aluminum cathode were sequentially deposited on the substrates under vacuum (≤ 6 x 10−5 Pa) at a deposition rate of ≤0.5 nm s−1 through a shadow mask defining a pixel size of 4.0 mm2 for each. The layer thicknesses and deposition rates were monitored in situ during deposition using an oscillating quartz thickness monitor. The J-V-L characteristics of the fabricated OLEDs were measured using a Keithley 2400 source meter and a CS-2000 spectroradiometer (Konica Minolta).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/1/eabe5769/DC1

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