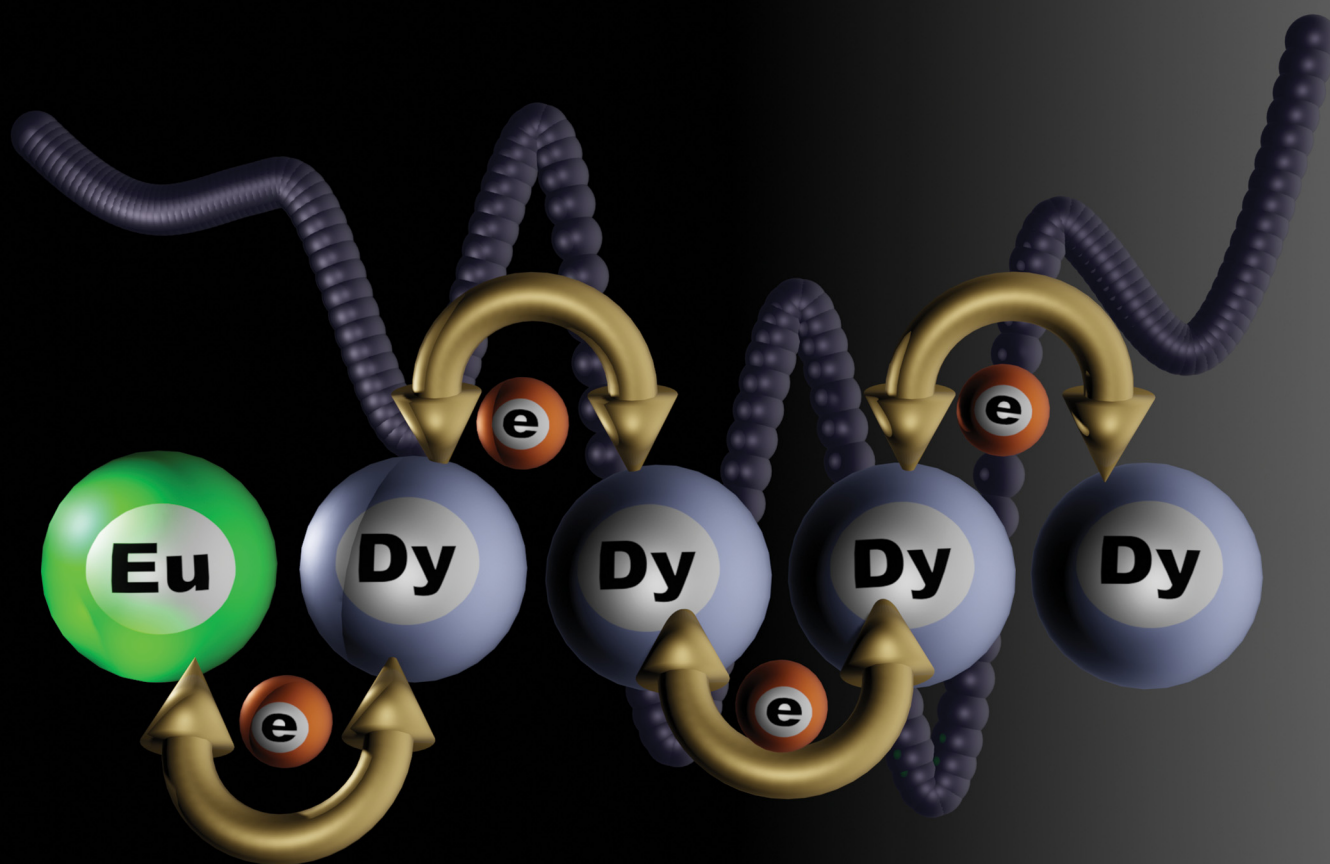


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**PAPER**

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Visualization of trap distribution in  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  revealed by simulations of luminescence changes in charging and emission of persistent luminescence and thermoluminescence based on a random walk model


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# Visualization of trap distribution in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ revealed by simulations of luminescence changes in charging and emission of persistent luminescence and thermoluminescence based on a random walk model†

 Ryusuke Koizumi, Ryoya Takahashi, Shigeki Yamada, Shingo Hattori  and Kazuteru Shinozaki \*

A stochastic analysis of the change in persistent luminescence (PersL) of  $\text{Sr}_{0.9}\text{Al}_2\text{O}_4:\text{Eu}_{0.01x}^{2+}, \text{Dy}_{(0.1-0.01x)}^{3+}$  (SAOED<sub>x</sub>,  $x = 2, 4, 5, 6, 8, \text{ and } 10$ ) based on a one-dimensional random walk model (1D RWM) is presented. In the RWM, the excited electron is treated as a particle and can hop stochastically between reservoirs aligned in a straight line. Simulations of changes in PersL and the charging process are performed to determine the hopping probabilities and the electron distributions in reservoirs. We predict potential energies of the electron reservoirs through simulations of the thermoluminescence (TL) spectra of SAOED<sub>x</sub> and present potential energy diagrams of the luminescence center and traps involved in PersL.

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## 1. Introduction

Afterglow or persistent luminescence (PersL) has fascinated researchers involved in science and technology of light since the discovery of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$  (SAOED) exhibiting outstanding long PersL over one night.<sup>1</sup> Initially, PersL of SAOED has been employed for clock face as an alternative to radio-active materials or road signs without electrical power in the dark. Recently, it has been applied to photosensitizers and *in vivo* luminescent materials for photodynamic therapy,<sup>2</sup> optical imaging,<sup>3</sup> thermo-luminescence dosimetry,<sup>4</sup> and solar cells.<sup>5</sup> In addition to the application studies, many fundamental studies on PersL materials have been conducted to develop brighter phosphors with much longer lasting luminescence.<sup>6–13</sup> The photoluminescence (PL) of SAOED originates from the 5d–4f electronic transition of  $\text{Eu}^{2+}$  as a dopant, where the excited electron in the 5d orbital is usually relaxed to the 4f orbital with a lifetime of around 1  $\mu\text{s}$  along with green luminescence.<sup>14</sup> For PersL, in contrast, the excited electron can be transferred to the host material by thermal or photoactivation and then be captured at trapping sites such as oxygen vacancies or defects, and thereafter the electron escaped from the trap by thermal

activation returns to the 5d orbital of  $\text{Eu}^{3+}$  to reproduce the excited  $^* \text{Eu}^{2+}$ , resulting in emission of luminescence. The co-dopant  $\text{Dy}^{3+}$  plays the role of a better electron trap, which contributes to the longer PersL compared to oxygen vacancies or defects. The excited electron may be tightly captured by  $\text{Dy}^{3+}$  due to the electrostatic attraction, that is,  $\text{Dy}^{3+}$  might be reduced to  $\text{Dy}^{2+}$  by analogy to the result that  $\text{Sm}^{2+}$  and  $\text{Ce}^{4+}$  were detected during the investigation of the electron de-trapping process for an PersL material  $\text{YPO}_4:\text{Ce}^{3+}, \text{Sm}^{3+}$ .<sup>15</sup>

Unlike PL, most PersL-decay features do not show a single-exponential curve. Therefore, the PersL decays have been frequently analysed using the double exponential equation,<sup>14</sup>

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2). \quad (1)$$

This equation consists of two exponential terms with the fast and slow decay times of  $\tau_1$  and  $\tau_2$ , respectively, where  $\tau_1$  may be related to the de-trapping from the oxygen vacancy with a shallow trap depth and  $\tau_2$  may originate from the deep trap of  $\text{Dy}^{3+}$ . Occasionally, the PersL decay is analysed using the triple exponential function,

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3). \quad (2)$$

In this case, the additional component would be attributed to another trap involved in the PersL decay. Thus, it seems hard to find the electron-transfer mechanism satisfying the triple-exponential decay feature.

Some mechanisms for PersL proposed in previous studies are based on a local model composed of a single luminescent

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centre and a single trap, where an excited electron is assumed to move back-and-forth between the luminescent centre and the trap in the PersL process.<sup>16</sup> In this model, the trap never captures two or more electrons, and the system of luminescence centres and traps is fully isolated and never interacts with others, that is, the electron cannot transfer to another trap in the adjacent system. In this situation, the observed PersL should always show a single-exponential decay curve, unless the electron transfer rates are slow compared with the time scale of PersL observation. On the other hand, a global model consisting of a luminescent centre, a trap, and the conduction band of host crystals has been applied to analyse the PersL decay.<sup>17</sup> The conduction band may be the pathway of electrons between the luminescent centre and the trap, and therefore the electrons involved in PersL would be distributed over the entire crystal in the PersL process. The electron transfer between the excited  $^*Eu^{2+}$  and the trap through the conduction band, based on the energy diagram with respect to the vacuum referred binding energy (VRBE) level,<sup>18,19</sup> has been taken into account for the PersL process. When electron de-trapping is caused by thermal activation, as per the Boltzmann distribution law, the ratio of the number of electrons in the luminescent centre and those in traps (oxygen vacancies and  $Dy^{3+}$ ) is constant. Even when the excited electrons at the luminescence centre are consumed during the PersL emission, the immediate compensation of electrons from traps within the time scale of PersL observation guarantees that the ratio remains as the constant value. From this consideration, the PersL decay curve should follow a single exponential, even if multi-traps are incorporated in the global model. Therefore, it is better to consider that the electron transfer between the luminescence centre and the trap is slow or comparable to the time scale of PersL observation, when the PersL decay curve can be analysed with a double- or multi-exponential function. Previously, we showed that plural traps contribute to the complicated PersL-decay feature of  $\beta-Zn_3(PO_4)_2:Mn^{2+}$  through the stochastic analysis using a one-dimensional random walk model (1D RWM).<sup>20</sup> In the 1D RWM, the excited electron can randomly hop back-and-forth between adjacent traps and occasionally hop into the luminescent centre at the edge of the trap array to emit PersL.<sup>20</sup> The simulation for electron migration based on the RWM was found to be simple yet significantly effective to reproduce the multi-exponential PersL decays.

For SAOED, we can observe the luminescence enhancement during continuous excitation corresponding to the charge of PersL.<sup>14</sup> In this charging process, the luminescence intensity keeps increasing and eventually reaches the maximum value when the increase rate of excited electrons by photoexcitation is balanced with the depletion rate of electrons due to PL and PersL.<sup>16</sup> The excited electrons seem to be continuously transferred to/from the host material and accumulated in traps until filling up. When the photoirradiation ceased, we can observe PersL alone from SAOED. Both PersL and charging processes should be accounted for by the electron transfer between the excited state of  $^*Eu^{2+}$  and the trap state of  $(Eu^{3+}-Trap^-)$ ,<sup>11</sup> where the electrons can move between the potential surfaces

of these states by overwhelming the activation state by thermal energy. Even when PersL disappeared due to the depletion of trapped electrons, luminescence can be recovered by other excited electrons squeezed out from deep traps by heating. The thermoluminescence (TL) spectrum, which is the luminescence observed at a variety of temperatures, provides information of trap depths in SAOED. A peak temperature in the TL spectrum is related to the trap depth, and the peak intensity is proportional to the number of escaped electrons from the trap.<sup>21,22</sup> Detailed analyses of the charging and PersL decay processes and the TL spectrum reveal the characteristics of dopants in SAOED and the mechanism of electron transfer between the luminescence centre and the trap involved in PersL.<sup>23</sup>

In this study, we show the effectiveness of the 1D RWM in simulating not only the non-exponential PersL decay curve of SAOED but also the charging process of PersL and TL. For the 1D RWM, we consider a train of multiple traps aligned in a straight line, where electrons can move back-and-forth between adjacent traps, and a luminescence centre is attached to the end of the trap line, where excitation of electrons and emission of luminescence take place. The simulation of the charging and PersL processes provides hopping probabilities among the luminescence centre and traps, corresponding to the electron transfer rates. Also, it provides evidence of electron population in traps, which helps to unveil the distribution of trap states in the SAOED crystal. In addition, the simulation of the TL spectrum provides the activation energy for each back-and-forth electron transfer process, which contributes to creating the energy diagram for traps involved in PersL for the SAOED crystal.

## 2. Simulation

### 2.1. A proposed mechanism of PersL emission

We propose a scheme for the PersL emission process based on the potential curves of Eu,  $^*Eu$ , and trapping sites (Ts) in SAOED as shown in Fig. 1. The horizontal axis corresponds to a reaction coordinate along the electron transfer.<sup>11</sup> We denote that the excitation rate of Eu is  $k_0$  and the relaxation rate of  $^*Eu$  is  $k_e$ . The electron transfer rates between potential curves are  $k_m$

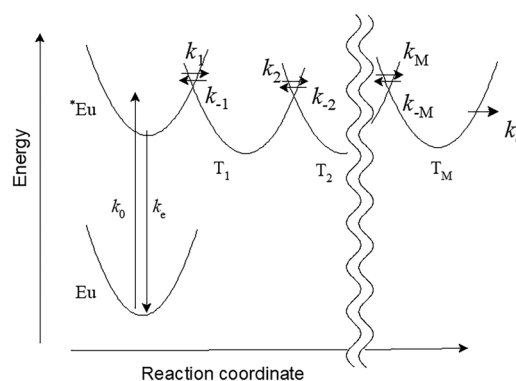
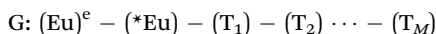


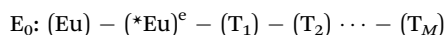
Fig. 1 A schematic energy diagram for Eu,  $^*Eu$ , and  $T_m$  ( $m = 1, 2, \dots, M$ ) for PersL of SAOED.  $k_m$  ( $m = \pm 1, \pm 2, \dots, \pm M$ ) are rate constants for electron transfer between potential wells.



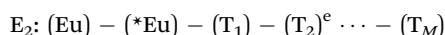
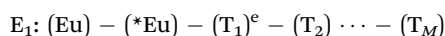
( $m = \pm 1, \pm 2, \dots, \pm M$ ), and the capturing rate at deep trap or quenching rate is  $k_q$ . Although the tunnelling between potential curves might be necessary to consider the PersL emission mechanism, we do not treat the tunnelling explicitly in the RWM because all electrons are postulated to be particles. When focused on a single electron, a ground state configuration can be represented as G,



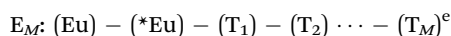
When  $*\text{Eu}$  is produced by photoexcitation, the electronic configuration can be represented as  $\text{E}_0$ ,



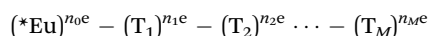
The excited electron in the 5d orbital of  $*\text{Eu}$  can either relax to the 4f orbital to emit luminescence resulting in the G configuration or get trapped at closest trap  $\text{T}_1$  which is represented as the  $\text{E}_1$  configuration. The electron at  $\text{T}_1$  ( $\text{E}_1$ ) can move to the next trap  $\text{T}_2$  ( $\text{E}_2$ ) or return to the luminescence centre  $*\text{Eu}$  ( $\text{E}_1$ ). The electron at  $\text{T}_2$  can move to  $\text{T}_3$  and so on,



⋮



Since there must be considerably many Eu ions in the bulk SAOED crystal, we should consider many sets of configurations  $\{n_0\text{E}_0, n_1\text{E}_1, n_2\text{E}_2, \dots, n_M\text{E}_M\}$  for the PersL process, where  $n_0, n_1, n_2, \dots, n_M$  are the numbers of respective excited configurations. We assume that this situation can be statistically equivalent to the following configuration with large numbers ( $n_0, n_1, n_2, \dots, n_M$ ) of electrons in each trap:



When  $n_0$  is decreased by luminescence emission, it will be compensated by the electron transfer from  $\text{T}_1$  to  $*\text{Eu}$ , which contributes to the elongation of the luminescence lifetime resulting in PersL. Since the emission intensity is proportional to the product of  $n_0$  and  $k_e$ , the simulation of PersL decay is equivalent to the determination of  $n_0k_e$  as a function of  $t$ . The simulation will provide not only  $n_0$  and  $k_e$  but also the other rate constants  $k_{\pm m}$  and the number of electrons ( $n_1, n_2, \dots, n_M$ ) in each trap. For the charging process, since  $n_m = 0$  ( $m = 0, 1, 2, \dots, M$ ) at the beginning, the photoexcitation contributes to an increase in  $n_0$  alone. After that, while  $n_0$  gradually decreases by the electron transfer to  $\text{T}_1$  and the relaxation to Eu, the continuous photoexcitation from Eu and the backward electron transfer from  $\text{T}_1$  contribute to an increase in  $n_0$ . Thus,  $n_0$  initially increases and eventually will reach the maximum value when the increase and decrease rates of  $n_0$  are balanced. This charging process should also be simulated from  $n_0k_e$  as a function of  $t$  using the rate constants determined by the PersL simulation. Since the electron transfer rate  $k_m$  corresponds to the de-trapping rate of electrons from the potential well, it

would strongly depend on temperature. Therefore, for simulations of the TL spectrum, the temperature dependence in the rate constant  $k_{\pm m}$  can be incorporated as

$$k_{\pm m} = k_{0,\pm m} \exp(-\Delta E_{\pm m}/k_B T), \quad (3)$$

where  $k_{0,\pm m}$  ( $m = 1, 2, \dots, M$ ) are pre-exponential factors,  $\Delta E_{\pm m}$  is trap depth or activation energy for each electron transfer process,  $k_B$  is Boltzmann's constant, and  $T$  is the absolute temperature. The simulation of the TL spectrum is equivalent to the prediction of  $n_0$  as a function of  $T$  and contributes to the determination of the activation energies for electron transfer ( $\Delta E_{\pm m}$ ).

## 2.2. A 1D random walk model (1D RWM) for the PersL

Based on the mechanism described above, we stochastically simulate the change in luminescence of the charging process, the non-exponential decay of PersL, and the TL spectrum using the 1D RWM as displayed in Fig. 2. The rectangle reservoirs being able to store electrons are aligned in a straight line, where each reservoir represents Eu,  $*\text{Eu}$ , or Ts. Eu is fixed at the left end, and  $*\text{Eu}$  is next to it. An array of Ts is set next to  $*\text{Eu}$ . We treat  $\text{Dy}^{3+}$  and other traps (oxygen vacancies or defects) as the same  $\text{T}_m$ . We assume that the electrons can move forward and backward between the very next reservoirs with certain probabilities, respectively, or can remain at the same reservoir. We introduce an electron-extinction path from  $\text{T}_M$  to represent the dropping in deep traps or the quenching. In this model, we introduce a probability  $p_m$  for each hopping between reservoirs instead of the electron-transfer rate constant  $k_m$ . Since the electron-transfer rate ( $k_m$ ) to overwhelm the activation barrier ( $\Delta E_m$ ) is represented as  $k_m = k_{m,0} \exp(-\Delta E_m/k_B T)$ , we can describe the hopping probability as

$$p_m = k_m/k_{m,0} = \exp(-\Delta E_m/k_B T). \quad (4)$$

For example, the electron at Eu can move to  $*\text{Eu}$  with a probability  $p_0$  ( $0 \leq p_0 \leq 1$ ) upon excitation. For the electron at  $*\text{Eu}$ , the probabilities of moving to Eu and  $\text{T}_1$  are  $p_e$  ( $0 \leq p_e \leq 1$ ) and  $p_1$  ( $0 \leq p_1 \leq 1$ ), respectively, and probability of remaining at  $*\text{Eu}$  is  $1 - p_e - p_1$ .

We define the number of electrons at reservoirs as  $N_0$  at  $*\text{Eu}$  and  $N_m$  at  $\text{T}_m$  ( $m = 1, 2, \dots, M$ ). For the random walk of electrons in the charging process, we initially prepare Eu with  $N$  electrons and the empty  $*\text{Eu}$  and Ts, that is,  $N_m^0 = 0$  ( $m = 0, 1, 2, \dots, M$ ). After the first step,  $Np_0$  electrons move to  $*\text{Eu}$  from Eu, but  $N(1 - p_0)$  electrons remain in Eu, that is,  $N_0^1 = Np_0$  and  $N_m^1 = 0$  ( $m = 1, 2, \dots, M$ ). After the second step, we can find

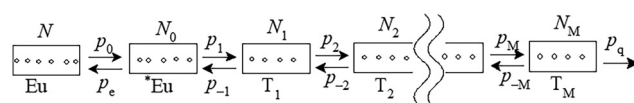


Fig. 2 Hopping probabilities ( $p_0, p_e, p_{\pm m}$ , and  $p_q$ ) and numbers of electrons ( $N, N_0$ , and  $N_m$ ) at reservoirs (Eu,  $*\text{Eu}$ , and  $\text{T}_m$ ) aligned in a straight line ( $m = 1 - M$ ). Boxes are electron reservoirs, and small circles are excited electrons involved in the PersL.



$N_0^2 = N(1 - p_0)p_0 + Np_0(1 - p_e) + Np_0(1 - p_1)$ ,  $N_1^2 = Np_0p_1$ , and  $N_m^2 = 0$  ( $m = 2, \dots, M$ ). The number of electrons  $N_m^n$  ( $m = 0, 1, 2, \dots, M$ ) at every reservoir after many steps ( $n$ ) can be obtained in similar ways, which are represented as functions of step number. By converting the step number ( $n$ ) into time ( $t$ ), we can predict the luminescence change by time from  $p_e N_0^n$ . For PersL, since the photoirradiation is ceased,  $p_0$  alone is needed to be  $p_0 = 0$ . After the first step, the numbers of electrons at \*Eu and  $T_1$  are  $N_0^1 = N_0(1 - p_e - p_1) + N_1p_{-1}$  and  $N_1^1 = N_0p_1 + N_1(1 - p_{-1} - p_2) + N_2p_{-2}$ , respectively. After the second step, the number of electrons at \*Eu is determined as  $N_0^2 = N_0^1(1 - p_e - p_1) + N_1^1p_{-1}$ . After  $n$  steps, we can analogously obtain the number of electrons at \*Eu as  $N_0^n = N_0^{n-1}(1 - p_e - p_1) + N_1^{n-1}p_{-1}$ . For both charging and PersL processes, we perform a curve-fitting of luminescence intensity of SAOED as a function of step number  $n$  to determine  $p_e, p_{\pm m}$  ( $m = 1, 2, \dots, M$ ),  $p_q$  and  $N_m$  ( $m = 0, 1, 2, \dots, M$ ). Since the observation of charging and PersL processes was conducted at room temperature  $T_{300} = 300$  K, the hopping probability can be described as  $p_{\pm}^{300}$ . Therefore, the probability at  $T$  can be represented as eqn (5) as a function of  $T$ ,

$$p_{\pm m}^T = p_{\pm}^{300} \exp(-\Delta E_{\pm m}/k_B)(1/T - 1/T_{300}). \quad (5)$$

Using  $p_{\pm m}^T$ , we performed a simulation of the TL spectrum for SAOED, which contributes to the determination of  $\Delta E_{\pm m}$ .

## 3. Results

### 3.1. Charging and PersL

We observed luminescence changes in the charging process for SAOED<sub>*x*</sub> ( $x = 2, 4, 5, 6, 8$ , and  $10$ ) which had been heated at  $500$  K for  $1$  h to de-trap electrons prior to the luminescence measurement. The luminescence intensities ( $I$ ) at  $520$  nm were recorded at time intervals of  $0.5$  s during the continuous photoirradiation with  $370$  nm light, and  $\log(I)$  was plotted with grey circles against  $\log(t)$  as shown in Fig. 3. As can be seen from the plots, the  $\log(I)$  values in the charging process exhibit complicated curves. For SAOED<sub>2</sub>, SAOED<sub>4</sub>, and SAOED<sub>5</sub>, each  $\log(I)$  increases, reaches the maximum value  $\log(I_{\max})$ , and then decreases. The increase in  $\log(I)$  at the early stage becomes reduced with increasing  $x$  and disappeared for SAOED<sub>6</sub>, SAOED<sub>8</sub>, and SAOED<sub>10</sub>. Still, the simulation, red lines, based on 1D RWM successfully reproduces the complex decay features of the charging processes for the entire samples. The SAOED<sub>*x*</sub> that underwent the charging process was employed for the PersL measurement. As shown in Fig. 3, the plot of each  $\log(I)$  against  $\log(t)$  for PersL shows an upward convex curve, suggesting that the PersL decays non-exponentially or multi-exponentially. The times when each PersL intensity becomes  $I_{\max}/100$  are  $t = 470$  s ( $x = 2$ ),  $195$  s ( $x = 4$ ),  $505$  s ( $x = 5$ ),  $116$  s ( $x = 6$ ),  $82$  s ( $x = 8$ ), and  $70$  s ( $x = 10$ ). Among them, the SAOED<sub>5</sub> likely shows the best performance for PersL. The red lines are simulated decay curves for the PersL and consistent with the experimental results.

Each hopping probability  $p_m$  ( $m = e, 1, -1, 2, -2, \dots$ , or  $q$ ) between reservoirs was restricted to be the same for the

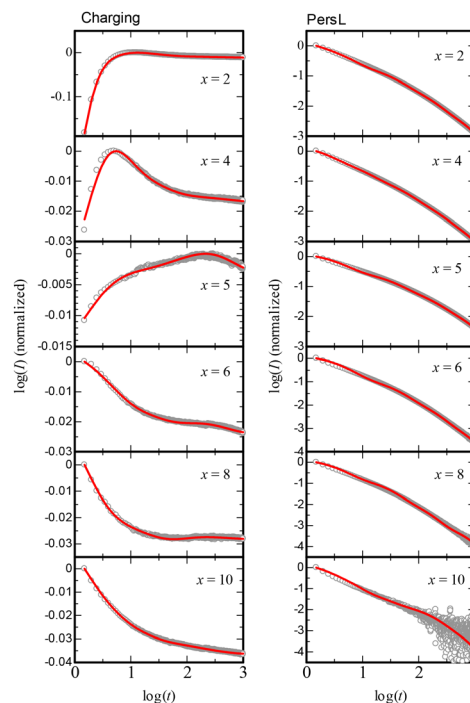


Fig. 3 (left) Changes in luminescence of SAOED<sub>*x*</sub> ( $x = 2, 4, 5, 6, 8$ , and  $10$ ) monitored at  $520$  nm in the charging process with the continuous irradiation of  $370$  nm at  $300$  K. (right) PersL of SAOED<sub>*x*</sub> ( $x = 2, 4, 5, 6, 8$ , and  $10$ ) monitored at  $520$  nm after the photoexcitation with  $370$  nm light for  $1$  min at  $300$  K. The relative integrated intensities of PersL for entire samples were  $5.10 \times 10^3$  ( $x = 2$ ),  $2.06 \times 10^3$  ( $x = 4$ ),  $1.54 \times 10^3$  ( $x = 5$ ),  $4.30 \times 10^2$  ( $x = 6$ ),  $1.15 \times 10^2$  ( $x = 8$ ), and  $1.00$  ( $x = 10$ ).

charging and PersL processes in the simulation and determined through curve fitting. Listed in Table 1 are  $p_m$  values converted to the hopping probabilities per second. It is noticed that the probabilities ( $p_5, p_{-5}, p_6, p_{-6}, p_7$ , and  $p_{-7}$ ) for the entire samples are almost zero, which suggests the very small contribution of reservoirs  $T_5, T_6$ , and  $T_7$  to the PersL of SAOED<sub>*x*</sub>. In other words, we can focus on \*Eu,  $T_1, T_2, T_3$ , and  $T_4$  to analyse the charging and PersL processes. The averaged

Table 1 Hopping probabilities between reservoirs predicted through the simulation of charging and PersL processes for SAOED<sub>*x*</sub> ( $x = 2, 4, 5, 6, 8$ , and  $10$ )

<i>x</i>	$p_e$	$p_1$	$p_2$	$p_3$	$p_4$	$p_5$	$p_6$	$p_7$	$p_q$
		$p_{-1}$	$p_{-2}$	$p_{-3}$	$p_{-4}$	$p_{-5}$	$p_{-6}$	$p_{-7}$	
2	0.312	0.218	0.166	0.009	0.002	0.000	0.074	0.083	0.068
		0.410	0.061	0.012	0.002	0.039	0.026	0.019	
4	0.338	0.157	0.042	0.007	0.003	0.001	0.083	0.032	0.186
		0.154	0.034	0.007	0.001	0.000	0.000	0.000	
5	0.233	0.115	0.369	0.012	0.002	0.000	0.099	0.032	0.067
		0.200	0.135	0.010	0.002	0.000	0.000	0.000	
6	0.280	0.064	0.109	0.006	0.001	0.000	0.099	0.032	0.059
		0.152	0.076	0.012	0.002	0.000	0.000	0.000	
8	0.328	0.082	0.294	0.007	0.001	0.000	0.100	0.032	0.188
		0.236	0.165	0.015	0.002	0.000	0.000	0.000	
10	0.469	0.164	0.077	0.019	0.001	0.000	0.099	0.032	0.000
		0.380	0.067	0.014	0.003	0.000	0.000	0.000	
Ave	0.330	0.116	0.178	0.010	0.001	0.001	0.096	0.032	0.111
		0.224	0.096	0.016	0.002	0.000	0.000	0.000	



hopping-probability from  $^*Eu$  to  $T_1$  ( $p_1$ ) is as half as the average probability  $p_e$ , corresponding to the intrinsic relaxation probability from excited  $^*Eu^{2+}$  in SAOED $_x$ . This result means that the 5d electron in the luminescence center easily transfers to the adjacent trap, leading to PersL for the SAOED $_x$  system. The simulation can provide the number of electrons  $N_m$  at reservoirs. Fig. S3 (ESI $^\dagger$ ) shows  $N_m$  ( $m = 0-6$ ) for SAOED $_x$  ( $x = 2, 4, 5, 6, 8, \text{ and } 10$ ), where  $N_0$  is normalized to unity. It is obvious that  $N_5$  and  $N_6$  are almost zero for the entire samples; there is no population of excited electrons.  $N_2, N_3,$  and  $N_4$  for SAOED $_5$  are larger than those for the other samples, respectively. This result seems to relate to the best performance in PersL for SAOED $_5$ .

### 3.2. Thermoluminescence

In Fig. 4, the thermoluminescence (TL) spectrum of each sample is plotted with grey circles from 200 to 400 K. We notice that the TL intensities of the entire samples increase from 0 at 200 K to the maximum value in the range of 250–300 K and decrease to 0 at 400 K. The peak of each spectrum would correspond to the trap depth in the corresponding sample. With increasing  $x$ , the peak temperature likely shifts to the low temperature region. It is suggested that the less the  $Eu^{2+}$  content ( $x$ ) in SAOED $_x$ , the deeper the trap depth. In addition, each spectral profile strongly depends on  $x$ . For example, we can see two peaks in the TL spectra of SAOED $_2$  and SAOED $_4$  but one for the others. We performed simulations of the TL spectra based on the RWM. In this simulation, the temperature dependence in hopping probability was incorporated using the following relationship:

$$p_{m,T} = p_{m,300} \exp(-(\Delta E_m/k_B)(1/T - 1/300)), \quad (6)$$

where  $p_{m,300}$  ( $m = 1, -1, 2, -2, \dots, q$ ) is the hopping probability at 300 K determined through the simulation of charging and

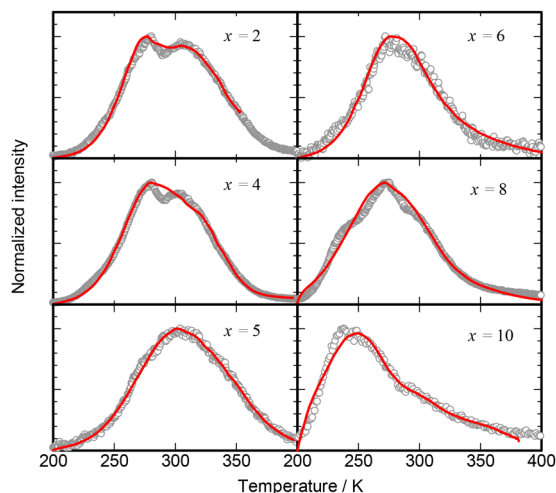


Fig. 4 TL spectra (grey circles) and their simulations (red lines) for SAOED $_x$  ( $x = 2, 4, 5, 6, 8,$  and  $10$ ). The samples were treated with the de-trapping at 500 K and the charging with 370 nm light for 10 min at 200 K. The luminescence of each sample was measured at 520 nm from 200 to 500 K with the increasing rate of  $1.03 \text{ K s}^{-1}$  after 10 min in the dark at 200 K.

PersL processes,  $k_B$  is Boltzmann's constant, and  $\Delta E_m$  is the activation energy for hopping between reservoirs. As shown in Fig. 4, the simulated TL spectra plotted with red lines are consistent with the experimental spectra of the entire samples. Specifically, the twin peaks for SAOED $_2$  are also well reproduced through the simulation. For each sample, we can prepare a potential energy diagram for the activation states and reservoirs from the resultant  $\Delta E_m$  as shown in Fig. 5, where the potential energies of them are relatively depicted with respect to that of  $^*Eu$ . For the entire samples, the energies of  $T_1$  are lower than those of  $^*Eu$ , and the activation energies  $\Delta E_1$  from  $^*Eu$  to  $T_1$  are  $12 \text{ kJ mol}^{-1}$  or less. These results strongly suggest that the 5d electron in the excited state of  $Eu^{2+}$  spontaneously transfers to the next trap  $T_1$ . The  $\Delta E_{-1}$  values for the backward hopping from  $T_1$  to  $^*Eu$  are  $35 \text{ kJ mol}^{-1}$  ( $x = 2$ ),  $34 \text{ kJ mol}^{-1}$  ( $x = 4$ ),  $27 \text{ kJ mol}^{-1}$  ( $x = 5$ ),  $29 \text{ kJ mol}^{-1}$  ( $x = 6$ ),  $24 \text{ kJ mol}^{-1}$  ( $x = 8$ ), and  $20 \text{ kJ mol}^{-1}$  ( $x = 10$ ). With an increase in the  $Eu^{2+}$  content  $x$ , the electrons at  $T_1$  seem to become easier to move back to  $^*Eu$ . This can reasonably account for the low temperature shift of peak temperature in TL when  $x$  is increased. For SAOED $_2$  and SAOED $_4$ , both  $\Delta E_2$  and  $\Delta E_{-2}$  are large, that is, the activation states between  $T_1$  and  $T_2$  are energetically high compared with the others. Most electrons are suggested to be accommodated in the relatively deep traps  $T_1$  and/or  $T_2$ , which might be related to the twin peaks in each TL spectrum of SAOED $_2$  and SAOED $_4$ . For SAOED $_5$ ,  $T_1, T_2,$  and  $T_3$  sink together, and the activation energy  $\Delta E_4$  for hopping from  $T_3$  to  $T_4$  is remarkably large. These results suggest that the most excited electrons are populated in traps of  $T_1$  through  $T_3$ . Although a high activation barrier of  $\Delta E_4$  is found for SAOED $_6$ , the excited electrons would be mostly accommodated in  $T_1$  because  $T_2$  and  $T_3$  are higher in energy than  $T_1$ . For SAOED $_8$ , it is considered that the electron populations at  $T_1$  and  $T_3$  are larger than the others. For SAOED $_{10}$ , it is characteristic that the reservoirs  $T_1$  through  $T_4$  act as sinks

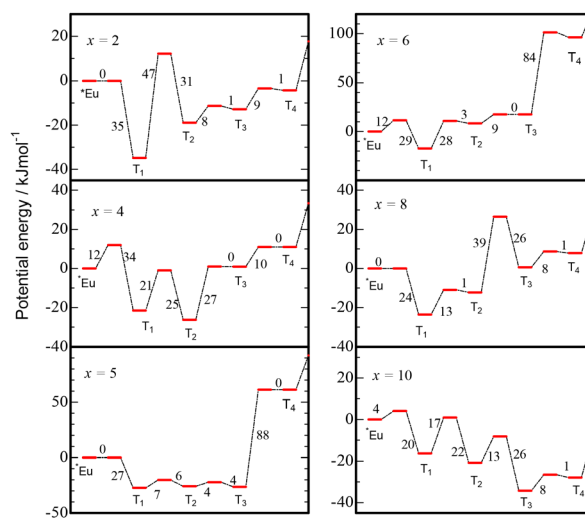


Fig. 5 Potential energy diagrams of  $^*Eu$  and  $T_m$  ( $m = 1-4$ ) for SAOED $_x$  ( $x = 2, 4, 5, 6, 8,$  and  $10$ ) predicted by the simulation based on the RWM. The numbers are  $\Delta E$  values in  $\text{kJ mol}^{-1}$  between the electron reservoir ( $^*Eu$  or  $T_m$ ) and the activation state, respectively.



compared with \*Eu. This result may suggest that the excited electrons are widely distributed over T<sub>1</sub> through T<sub>6</sub>.

## 4. Discussion

### 4.1. Multiple traps

X-ray crystallography revealed that there are two Sr<sup>2+</sup> sites (Sr1 and Sr2) in host crystal SrAl<sub>2</sub>O<sub>4</sub>, where both Sr<sup>2+</sup> sites are crystallographically nonequivalent to each other yet very similar in coordination structure.<sup>24</sup> These Sr<sup>2+</sup> sites in the SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> crystal can be exchanged with dopant Eu<sup>2+</sup> due to their similar ionic radii of 1.21 Å (Sr<sup>2+</sup>) and 1.20 Å (Eu<sup>2+</sup>)<sup>25</sup> and the same electric charges. Since the electronic configuration of excited Eu<sup>2+</sup> is represented as 4f<sup>6</sup>5d<sup>1</sup> involving the 5d orbital, the excited energy is sensitive to the difference in coordination geometry. Therefore, the modulation of coordination number of Eu<sup>2+</sup> by O atoms by varying the SrO/Al<sub>2</sub>O<sub>3</sub> ratio of host material results in the drastic change in the emission peak from 275 nm for SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> to 467 nm for Sr<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>:Eu<sup>2+</sup>.<sup>26</sup> SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> emits blue and green luminescence peaking at 455 and 520 nm, respectively, which are assigned to the emission from \*Eu<sup>2+</sup> at Sr1 and Sr2.<sup>26,27</sup> The DFT calculation predicted that co-dopant Dy<sup>3+</sup>, as well as Eu<sup>2+</sup>, occupies the most energetically stable Sr<sup>2+</sup> site.<sup>27</sup> This is consistent with the result of field-emission scanning electron microscopy (FE-SEM) that Eu<sup>2+</sup> and Dy<sup>3+</sup> are evenly distributed in the SrAl<sub>2</sub>O<sub>4</sub> host.<sup>28</sup> On the other hand, another SEM measurement suggests the agglomeration of Dy<sup>3+</sup> at grain boundaries in SrAl<sub>2</sub>O<sub>4</sub>.<sup>11</sup> Given these reports for the SAOED structure, we should consider that there are a variety of coordination structures around Eu<sup>2+</sup> and Dy<sup>3+</sup> for SAOED depending on its crystal structure and the contents of Eu<sup>2+</sup> and Dy<sup>3+</sup>. Especially, the variation in the coordination structure around Dy<sup>3+</sup> will result in a variety of trap depths contributing to the multi-exponential PersL decay. Despite the complex trap system in SAOED, the simple 1D RWM is effective for the simulation of the charging and PersL processes and the TL spectra and contributes to the prediction of the traps and activation states in the SAOED crystals. The validity of the 1D trap array assumption would be rationally accounted for by the electron hopping path which can be uniquely determined when the hopping preferentially occurs between the closest traps in the crystal.

### 4.2. Analysis using the triple-exponential function

For SAOED<sub>2</sub>, we observed the rise-and-decay curve for the change in luminescence intensity during the charging process as mentioned above. In accordance with the global system consisting of a single \*Eu-trap system with a conduction band, the luminescence rise at the early stage is accounted for by the increase in the number of excited electrons in the \*Eu-trap system due to the continuous photoirradiation. When a curve fitting using an equation incorporating the rise component was carried out (Fig. S4, ESI<sup>†</sup>), we needed two additional decay components to match the simulation with the experimental result. This strongly suggests that the number of excited electrons at the luminescence centre \*Eu does not remain constant

even after filling them up. In this simulation, we employed eqn (7),

$$I_c = I_{c1} \exp(-t/\tau_{c1}) + I_{c2} \exp(-t/\tau_{c2}) + I_{c3} \exp(-t/\tau_{c3}) + I_{c0} \quad (7)$$

where  $\tau_{c1}$ ,  $\tau_{c2}$ , and  $\tau_{c3}$  are lifetimes,  $I_{c1}$ ,  $I_{c2}$ , and  $I_{c3}$  are pre-exponential factors, and  $I_{c0}$  is a constant. From the best fit, we determined  $\tau_{c1} = 44$  s,  $\tau_{c2} = 5.1 \times 10^4$  s, and  $\tau_{c3} = 1.3$  s,  $I_{c1} = 0.025$ ,  $I_{c2} = 0.26$ , and  $I_{c3} = -1.1$ , and  $I_{c0} = 0.72$ , as listed in Table S2 (ESI<sup>†</sup>). The electron filling process represented by the rise component is likely completed within  $\tau_{c3} = 1.3$  s in the present case. The decay components would correspond to electron transfer from the luminescence centre to traps and/or leaking electrons from the \*Eu-trap system along with no luminescence such as quenching or dropping into deep traps. It might be essential that the electron transfer rate from \*Eu to traps involved in PersL of SAOED<sub>2</sub> is slow. At the later stage showing the constant intensity  $I_{c0} = 0.72$ , the electron filling rate is likely balanced with the electron consuming rates due to the leaking and the luminescence emission. For PersL of SAOED<sub>2</sub>, Fig. S4 (ESI<sup>†</sup>) shows that a curve fitting using eqn (8) provides the best result and affords  $\tau_{p1} = 5.0$  s (89%),  $\tau_{p2} = 65$  s (10%), and  $\tau_{p3} = 430$  s (1%),

$$I_p = I_{p1} \exp(-t/\tau_{p1}) + I_{p2} \exp(-t/\tau_{p2}) + I_{p3} \exp(-t/\tau_{p3}). \quad (8)$$

This triple exponential function strongly suggests that there are at least three electron-trapping sites or reservoirs involving the PersL decay of SAOED<sub>2</sub>. For the other samples, the simulation using eqn (7) and (8) successfully reproduced the luminescence changes in the charging and PersL as shown in Fig. S4 (ESI<sup>†</sup>). The parameters determined by the simulation are listed in Table S2 (ESI<sup>†</sup>). The resultant  $\tau_{p1}$ ,  $\tau_{p2}$ , and  $\tau_{p3}$  for PersL of each sample are roughly the same:  $\tau_{p1} = 3\text{--}7$  s (ca. 90%),  $\tau_{p2} = 27\text{--}71$  s (ca. 10%), and  $\tau_{p3} = 170\text{--}450$  s (ca. 1%). No remarkable change in lifetimes is observed. On the other hand, for the charging process, although the result for SAOED<sub>4</sub> is similar to that for SAOED<sub>2</sub>, the others are different. For SAOED<sub>5</sub>, two rise components,  $I_{c2} = -0.025$  ( $\tau_{c2} = 3.0$  s) and  $I_{c3} = -0.0083$  ( $\tau_{c3} = 70$  s), are needed to fit the experimental luminescence change. For SAOED<sub>6</sub> and SAOED<sub>8</sub>, the luminescence change in the charging process can be reproduced with two decay components, since the third component is negligibly small. For SAOED<sub>10</sub>, three decay components are needed to reproduce the luminescence change. Although we can estimate lifetimes for the charging and PersL processes based on eqn (7) and (8), it seems hard to clarify the role of traps in the luminescence behaviours in the entire SAOED<sub>x</sub>, even when we take multi-traps in a SAOED crystal into account for the PersL decay and the charging process. In contrast, it is significant that the stochastic analysis using the RWM can predict the energy diagram of \*Eu and traps, the electron hopping probabilities between traps, and the electron distribution in traps for the entire samples.

### 4.3. Trap depth from TL spectra

According to the literature,<sup>29–31</sup> we can determine the trap depth ( $E$ ) for each SAOED<sub>x</sub> from the corresponding TL spectrum, assuming the single luminescence centre-single trap



**Table 2** Trap depths ( $E_1$  and  $E_2$  in  $\text{kJ mol}^{-1}$ ) for SAOED $_x$  ( $x = 2, 4, 5, 6, 8,$  and  $10$ ) evaluated from the TL spectra, obtained from eqn (3) and (4), respectively.  $\Delta E_d$  values in  $\text{kJ mol}^{-1}$  are determined from the potential energies of deepest reservoirs for SAOED $_x$ , respectively, with respect to that for \*Eu

$x$	2	4	5	6	8	10
$E_1$ ( $\text{kJ mol}^{-1}$ )	53.3	41.3	32.6	38.6	73.5	84.4
$E_2$ ( $\text{kJ mol}^{-1}$ )	63.5	40.5	68.5	64.4	93.6	99.8
$\Delta E_d$ ( $\text{kJ mol}^{-1}$ )	35	26	27	17	24	34

system. To do so, we created a plot of  $\ln(T^2/\beta)$  vs.  $1/k_B T$  in accordance with Hoogenstraaten's equation:<sup>29</sup>

$$\ln\left(\frac{T^2}{\beta}\right) = \frac{E_1}{k_B T} + \ln\left(\frac{E_1}{k_B s}\right) \quad (9)$$

where  $T$  is the peak temperature resulting from a TL spectrum,  $k_B$  is Boltzmann's constant,  $\beta$  is the heating rate, and  $s$  is the oscillating factor. The slope of the plot provides a trap depth  $E_1$  for each sample, which is listed in Table 2. Alternatively, we can also determine the trap depth from eqn (10) derived from the fact that the change in  $\beta$  brings the shift of the peak temperature of the TL spectrum.<sup>30,31</sup>

$$T_2 = T_1 \left(\frac{\beta_2}{\beta_1}\right)^{k_B T_1 / E_2} \quad (10)$$

The trap depths ( $E_2$ ) determined from this equation are listed in Table 2. The resultant  $E_1$  and  $E_2$  are in the range of 30–100  $\text{kJ mol}^{-1}$ , which are consistent with the values reported by other researchers.<sup>22</sup> However, it seems that there is no relationship between the trap depth and the Eu<sup>2+</sup> content  $x$  in SAOED $_x$ . Especially, the deepest  $E_1$  and  $E_2$  are obtained from both methods for SAOED<sub>10</sub>, which is inconsistent with the physical intuition that the lower the peak temperature in the TL spectrum, the shallower the trap depth. Table 2 lists energy gaps  $\Delta E_d$  between \*Eu and the deepest trap in SAOED $_x$  obtained through the analyses for TL spectra using the RWM.  $\Delta E_d$ , the largest being 35  $\text{kJ mol}^{-1}$  for SAOED<sub>2</sub> among them, decreases and increases with increasing  $x$ . For SAOED<sub>10</sub>,  $\Delta E_d$  is comparable to that for SAOED<sub>2</sub>. It is interesting that this trend in  $\Delta E_d$  against  $x$  is similar to that in  $E_1$ .

## 5. Conclusions

We employed SAOED $_x$  ( $x = 2, 4, 5, 6, 8,$  and  $10$ ) containing 10% dopants (Eu<sup>2+</sup> and Dy<sup>3+</sup>) in host crystal SrAl<sub>2</sub>O<sub>4</sub> to produce a large amount of electron traps owing to Eu<sup>2+</sup>, Dy<sup>3+</sup>, oxygen vacancies, and defects. It should be noted that although the 1D trap array must be far apart from the actual arrangement of electron traps of Eu<sup>2+</sup>, Dy<sup>3+</sup>, oxygen vacancies, and defects in SAOED $_x$  crystals, the simulation based on the 1D RWM successfully reproduced the complicated luminescence changes in charging and PersL and the TL spectrum for each SAOED $_x$ . The resultant energy diagram of the luminescence centre and traps for each sample is simple and helpful for understanding

the PersL of SAOED $_x$  with a complicated trap system. The RWM is simple yet effective to visualize the picture that electrons migrate in the SAOED crystal with a variety of traps.

## Author contributions

R. Koizumi and R. Takahashi conducted the preparation and identifications of materials, the luminescence measurements, and the simulation. S. Hattori and S. Yamada contributed to the experimental work and participated in discussions. K. Shinozaki supervised this project and wrote the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the ESI.†

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