New Ce$^{3+}$-Activated Thiosilicate Phosphor for LED Lighting—Synthesis, Luminescence Studies, and Applications

Szu-Ping Lee,† Chien-Hao Huang,‡ Ting-Shan Chan,§ and Teng-Ming Chen*†

†Phosphors Research Laboratory, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan
‡Material and Chemical Research Laboratories, ITRI, Hsinchu 30011, Taiwan
§National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

ABSTRACT: A new Ce$^{3+}$-activated thiosilicate phosphor, BaLa$_2$Si$_2$S$_8$:Ce$^{3+}$, was synthesized by using solid-state methods in a fused silica ampule and found to crystallize in the structure type of La$_2$PbSi$_2$S$_8$. The crystal structure has been characterized by synchrotron X-ray diffraction and refined with Rietveld methods. This novel cyan-emitting phosphor can be excited over a broad range from UV to blue light (380−450 nm) and generates a broadband emission peaking at 471 nm with a quantum efficiency of 36%. Nonradiative transitions between Ce$^{3+}$ ions in BaLa$_2$Si$_2$S$_8$:Ce$^{3+}$ have also been demonstrated to be attributable to dipole−dipole interactions, and the critical distance was calculated to be 17.41 Å. When BaLa$_2$Si$_2$S$_8$:Ce$^{3+}$ phosphor was utilized to incorporate with yellow-emitting (Sr,Ca)$_2$SiO$_4$:Eu$^{2+}$ phosphor and red-emitting CaAlSiN$_3$:Eu$^{2+}$ phosphor on a 430 nm blue LED chip, a warm white light LED device with color rendering index of ∼96 was obtained. The results indicate that cyan-emitting BaLa$_2$Si$_2$S$_8$:Ce$^{3+}$ can serve as a potential phosphor for incorporation in fabrication of solid-state lighting. The preparation, spectroscopic characterization, quantum efficiency, decay lifetime, thermal-quenching behavior, and related LED device data are also presented.

KEYWORDS: BaLa$_2$Si$_2$S$_8$:Ce$^{3+}$, thiosilicate phosphor, photoluminescence, white-light LED

INTRODUCTION

Since the invention of the blue light-emitting InGaN-based light emitting diode (LED) in the early 20th century, remarkable progress has been made in the development of commercially realized efficient white light LEDs (WLEDs). By the combination of blue emission from the InGaN-based LED chips and yellow emission from the down-conversion of Y$_3$Al$_5$O$_12$:Ce$^{3+}$ (YAG:Ce)-based phosphors, the generated white light has already exceeded that of incandescent lamps and is competitive with conventional fluorescent lamps. WLEDs are energy-efficient, life-durable, and environmentally friendly in comparison to conventional light sources; however, the color quality of WLEDs still requires improvement with respect to tunability of the white hue, color temperature, and color rendering. In particular, these properties are closely correlated to the general illumination. For most of the currently applied phosphors in the WLEDs system, they do not reach the optimal requirements for white light and show poor color rendition in the red spectral region. Therefore, to attain the optical requirements for white light, many new phosphors are reported in order to overcome the aforementioned drawbacks and to obtain suitable luminescent material for phosphor-converted white light emitting diodes (pc-WLEDs).

The luminescence properties of binary A$^{12}$S (A = Ca, Sr, Ba, Zn) and ternary A$^{12}$B$^{III}$S$_4$ (B = Al, Ga, In) sulﬁde compounds doped with various transition metals (such as Cu, Ag, and Pb) or rare earth ions (Ce$^{3+}$ and Eu$^{2+}$) have been investigated for more than thirty years. These compounds have attracted significant interest due to their capability for lighting and display applications. Moreover, many studies have reported the photoluminescence (PL) characteristics of sulﬁde phosphors for compensating the red color deﬁciency and producing high color rendering white light in the WLEDs. Recently, some luminescent oxysulﬁde-based phosphors have been developed; Kuo et al. reported that the CaZnOS:Eu$^{2+}$ phosphor exhibits a broad absorption band and excellent color purity as a complementary red-emitting component. Yu et al. presented the luminescence properties of the CaAl$_2$S$_4$:Eu$^{2+}$/Ce$^{3+}$ thioaluminate phosphor. Parmentier et al. reported a new family of M$_2$Si$_2$Eu$^{2+}$ (M = Ca, Sr, and Ba) thiosilicate...
phosphors and its tunable PL characteristics by adjusting the alkaline earth ratio. Although sulfide phosphors have met with a predicament in terms of rapid degradation of luminescent intensity because of a relatively unstable thermal chemical property when compared to oxides, the low manufacturing temperature and superior optical variety still make sulfides attractive.

For most phosphors doped with Ce\(^{3+}\), a parity-allowed 5d→4f emission ranging from ultraviolet to red color is shown depending upon the host lattice and the site size, site symmetry, and coordination number. In fact, the emission color of Ce\(^{3+}\) can also be controlled in the desired region of the spectrum by changing the crystal field strength.\(^{22-24}\) For example, the optical properties of Ce\(^{3+}\) dopant in Ca(Si,Al)N\(_2\):Ce\(^{3+}\)\((\text{red})\),\(^{25}\) (La,Gd)Sr\(_2\)AlO\(_5\):Ce\(^{3+}\)\((\text{yellow})\),\(^{26}\) and (Ca,Sr)Sc\(_2\)O\(_4\):Ce\(^{3+}\)\((\text{green})\)\(^{27}\) phosphors have been investigated. In this research, we have discovered and report a new Ce\(^{3+}\)-activated BaLa\(_2\)Si\(_2\)S\(_8\) thiosilicate phosphor, which was found to crystalize in the structure type of La\(_2\)PbSi\(_2\)S\(_8\).\(^{28}\) For the first time, we investigated the crystal structure of BaLa\(_2\)Si\(_2\)S\(_8\) lattice obtained from Rietveld refinement via synchrotron X-ray diffraction (SXRD) patterns and reported the luminescent properties of the BaLa\(_2\)Si\(_2\)S\(_8\):Ce\(^{3+}\) phosphor. This new phosphor can be excited by light in the n-UV to blue region and shows cyan emission. In addition, the temperature dependence of the LED device using BaLa\(_2\)Si\(_2\)S\(_8\):Ce\(^{3+}\) phosphor with a blue LED chip was investigated to demonstrate the applicability of the BaLa\(_2\)Si\(_2\)S\(_8\):Ce\(^{3+}\) phosphor as a color conversion material.

### EXPERIMENTAL SECTION

**Materials.** The powder samples of Ba\(_{(La_{1-x}Ce_{x})_{2}}Si_{2}S_{8}\) were synthesized by solid-state reactions using La\(_2\)S\(_3\) (Alfa, 99%), BaS (Alfa, 99.7%), Ce\(_2\)S\(_3\) (Alfa, 99.9%), Si powder (Alfa, 99.999%), and S powder (Acros, 99.999%) as raw materials. The stoichiometric amounts of the starting materials were thoroughly mixed and loaded into a vertically positioned fused silica ampule, fully evacuated to 10\(^{-3}\) Torr, and sealed off under a dynamic vacuum. The fused silica ampule was heated at 5 °C/min to 1000–1100 °C for 6–8 h in a furnace and then cooled down slowly to room temperature. The chemical reaction can be summarized in the following:

\[
\text{BaS} + (1 - x)\text{La}_{2}\text{S}_{3} + x\text{Ce}_{2}\text{S}_{3} + 2\text{Si} + 4\text{S} \rightarrow \text{Ba(La}_{1-x}\text{Ce}_{x})_{2}\text{Si}_{2}\text{S}_{8}
\]

(1)

The pc-WLEDs devices were fabricated using commercial blue InGaN-based LEDs (\(\lambda_{\text{max}} = 430\) nm) with an intimate mixture of silicone resin and phosphor blending of cyan-emitting BaLa\(_2\)Si\(_2\)S\(_8\):Ce\(^{3+}\), yellow-emitting (Sr,Ca)\(_2\)SiO\(_4\):Eu\(^{2+}\)\(^{29}\) commodity (Inmatix-Y4453), and red-emitting CaAlSiN\(_3\):Eu\(^{2+}\)\(^{30}\) commodity (Mitsubishi-BR-102C) in the ratio of 6:3:2.

**Characterization.** SXRD profiles were recorded at the BL01C2 beamline of National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan, equipped with a Mar345 imaging plate and using an X-ray wavelength of 0.774908 Å. X-ray Rietveld refinements were conducted using the General Structure Analysis System (GSAS) software.\(^{31,32}\) The morphology and energy-dispersive X-ray spectroscopy (EDS) spectrum were measured with a JEOL JSM-7401F conventional thermal field-emission scanning electron microscope. The diffuse reflection (DR) spectra were measured with a Hitachi 3010 double-beam UV-vis spectrometer (Hitachi Co., Tokyo, Japan) equipped with a 060 mm integrating sphere. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded with a Spex Fluorolog-3 spectrophotometer (Jobin Yvon Inc./Specs) equipped with a 450 W Xe lamp and analyzed by a Jobin-Yvon spectrometer HR460 with multichannel charge-coupled device detector. The luminescence decay lifetime were measured on a tunable nanosecond optical-parametric-oscillator/Q-switch-pumped YAG:Nd\(^{3+}\) laser system (Ekspla). The quantum efficiency (QE) was measured by an integrating sphere whose inner face was coated with Spectralon equipped with a spectrophotometer (Horiba Jobin-Yvon Fluorolog 3–2–2). The thermal luminescence (TL) quenching was tested using a heating apparatus (THMS-600) in combination with PL equipment. The Commission Internationale de l’Eclairage (CIE) chromaticity coordinates were determined by a Laiko DT-100 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan). The electroluminescence (EL) spectra were recorded under a forward bias current 350 mA and measured by using a SphereOptics integrating sphere with LED measurement starter packages (Onset, Inc.).

### RESULTS AND DISCUSSION

**Structural Characterizations and Crystallographic Parameters of the BaLa\(_2\)Si\(_2\)S\(_8\) and Ba(La\(_{0.94}\text{Ce}_{0.06}\))\(_2\)Si\(_2\)S\(_8\) Phosphors.** To approach a dependable approximation of the actual crystal structure, the isotypic single-crystal structure data of La\(_2\)PbSi\(_2\)S\(_8\) were used as a starting model. LaPb\(_2\)Si\(_2\)S\(_8\) is reported with crystallographic data by Gulay et al.\(^{28}\) With the similar size of ionic radii in eightfold coordinated Pb\(^{2+}\) ion and alkaline-earth metal(I), such as Ba\(^{2+}\) ion,\(^{33}\) we can demonstrate the adaptability of a new phosphor host BaLa\(_2\)Si\(_2\)S\(_8\).

The Rietveld refinements are accomplished for BaLa\(_2\)Si\(_2\)S\(_8\) and Ba(La\(_{0.94}\text{Ce}_{0.06}\))\(_2\)Si\(_2\)S\(_8\) phosphors from the observed SXRD patterns (Figure 1) and show that the final converged weighted profiles of \(R_{wp}\) are 9.18% and 8.77%, respectively, indicating the single phase with no unidentified diffraction peaks from impurity. Both structures are found to crystallize hexagonally...
Table 1. Structural Parameters of BaLa$_2$Si$_2$S$_8$ and Ba(La$_{0.94}$Ce$_{0.06}$)$_2$Si$_2$S$_8$ of Rietveld Refinement from SXRD Data at Room Temperature$^a$

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyck.</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>S.O.F</th>
<th>U$_{iso}*100$</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>S.O.F</th>
<th>U$_{iso}*100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba 18e</td>
<td>0.34600(16)</td>
<td>0.01273(16)</td>
<td>0.0833</td>
<td>0.333</td>
<td>5.55(6)</td>
<td>0.34628(16)</td>
<td>0.01296(16)</td>
<td>0.0833</td>
<td>0.333</td>
<td>5.44(6)</td>
<td></td>
</tr>
<tr>
<td>La 18e</td>
<td>0.34600(16)</td>
<td>0.01273(16)</td>
<td>0.0833</td>
<td>0.333</td>
<td>5.55(6)</td>
<td>0.34628(16)</td>
<td>0.01296(16)</td>
<td>0.0833</td>
<td>0.333</td>
<td>5.44(6)</td>
<td></td>
</tr>
<tr>
<td>Si 12c</td>
<td>0.3333</td>
<td>0.3333</td>
<td>1.000</td>
<td>4.92(25)</td>
<td>0.3333</td>
<td>0.3012(5)</td>
<td>0.3333</td>
<td>0.3012(5)</td>
<td>0.3012(5)</td>
<td>4.95(17)</td>
<td></td>
</tr>
<tr>
<td>S1 12c</td>
<td>0.3333</td>
<td>0.3333</td>
<td>1.000</td>
<td>4.92(25)</td>
<td>0.3333</td>
<td>0.3012(5)</td>
<td>0.3333</td>
<td>0.3012(5)</td>
<td>0.3012(5)</td>
<td>4.95(17)</td>
<td></td>
</tr>
<tr>
<td>S2 36f</td>
<td>0.4348(5)</td>
<td>0.3090(5)</td>
<td>0.01932(14)</td>
<td>1.000</td>
<td>5.19(18)</td>
<td>0.4347(4)</td>
<td>0.3012(5)</td>
<td>0.01945(14)</td>
<td>1.000</td>
<td>5.19(18)</td>
<td></td>
</tr>
<tr>
<td>Ce 18e</td>
<td>0.34606(16)</td>
<td>0.01273(16)</td>
<td>0.0833</td>
<td>0.333</td>
<td>5.55(6)</td>
<td>0.34628(16)</td>
<td>0.01296(16)</td>
<td>0.0833</td>
<td>0.333</td>
<td>5.44(6)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Hexagonal; space group: R$ar{3}$c (No. 167); lattice parameters: a and c in pm, V in 10$^6$ pm$^3$; U$_{iso}$ in Å$^2$; α = β = 120º, γ = 90º; T = 298 K; Z = 6; beamline 01C2 of NSRRC, λ = 0.77491 Å; Site Occupancy Fraction (S.O.F.).

Table 2. Selected Interatomic Bond Distances$^b$ of BaLa$_2$Si$_2$S$_8$ and Ba(La$_{0.94}$Ce$_{0.06}$)$_2$Si$_2$S$_8$ at Room Temperature

<table>
<thead>
<tr>
<th>BaLa$_2$Si$_2$S$_8$</th>
<th>Ba(La$<em>{0.94}$Ce$</em>{0.06}$)$_2$Si$_2$S$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ba/La)-S1</td>
<td>312.06(8) (2x)</td>
</tr>
<tr>
<td>(Ba/La)-S2</td>
<td>292.55(4) (2x)</td>
</tr>
<tr>
<td>(Ba/La)-S1$^4$</td>
<td>334.45(4) (2x)</td>
</tr>
<tr>
<td>(Ba/La)-S2$^4$</td>
<td>304.7(4) (2x)</td>
</tr>
<tr>
<td>(Ba/La)-Si</td>
<td>381.4(6) (2x)</td>
</tr>
<tr>
<td>(Ba/La)-Si$^2$</td>
<td>377.6(5) (2x)</td>
</tr>
</tbody>
</table>

$^b$Bond distances in pm.

Spectroscopic Study of the Ba(La$_{1-x}$Ce$_x$)$_2$Si$_2$S$_8$ Thiosilicate Phosphor. Figure 3 shows the DR spectrum of as-synthesized polycrystalline BaLa$_2$Si$_2$S$_8$ and Ba(La$_{0.94}$Ce$_{0.06}$)$_2$Si$_2$S$_8$. For the BaLa$_2$Si$_2$S$_8$ host, the DR spectrum shows a status of high reflection in the wavelength ranging from...
respectively, at 465 nm (21,505 cm\(^{-1}\)).

The relative intensity in both PLE and PL spectra varies with different Ce\(^{3+}\) dopant concentrations, and an optimal value of \(x = 0.06\) (ca. 6 mol %) is obtained for so-called critical concentration (\(x_c\)). Because each activator ion is introduced solely into one site, there is, on the average, one activator per \(V/x_cN\) when considering the concentration quenching caused by the energy transfer mechanisms, such as exchange interaction, radiation reabsorption, or multipole–multipole interaction. The critical energy transfer distance (\(R_c\)) is approximately equal to twice the radius of a sphere with the volume,

\[
R_c \approx 2 \left( \frac{3V}{4\pi x_c N} \right)^{1/3}
\]

where \(V\) represents the volume of unit cell, \(x_c\) the critical dopant concentration, and \(N\) the number of total Ce\(^{3+}\) sites in the unit cell. In this case, \(V = 1989.13\) Å\(^3\), \(N = 6\), and \(x_c = 0.12\) (ca. 6 mol %). Thus, the \(R_c\) of Ce\(^{3+}\) was calculated to be 17.41 Å. If the rapid migration of Ce\(^{3+}\) ion happens, quenching tends to be proportional to the Ce\(^{3+}\) concentration, which is not being observed in PL spectra. Since the exchange interaction takes place generally in the forbidden transition (the \(R_c\) is typically \(\sim 5\) Å), the PLE and PL spectra do not overlap very well. Therefore, we can infer that the nonradiative concentration quenching between two nearest Ce\(^{3+}\) centers occurs via electric multipolar interactions based on the Dexter theory. For the emission intensity per activator concentration, the following equation can be described

\[
I/x = \frac{k}{1 + \beta(x)^{\theta/3}}
\]

where \(I\) represents the quenching intensity; \(x\) represents Ce\(^{3+}\) concentration; \(k\) and \(\beta\) represent constants for individual electric multipolar interactions; \(\theta = 6\), 8, and 10 demonstrate, respectively, the dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions. As represented in Figure 4b, the correlation between \(\log(I/x)\) with \(\log(x)\) can be fitted linearly within PL spectra of Ba(La\(_{1−x}\)Ce\(_x\))\(_2\)Si\(_2\)S\(_8\) (\(x = 0.01, 0.02, 0.04, 0.06, 0.08, \) and 0.10) and the value \(\theta\) was determined to be 5.34 from the slope (\(\theta/3\)). In particular, the calculated value for Ba(La\(_{1−x}\)Ce\(_x\))\(_2\)Si\(_2\)S\(_8\) is close to 6, which implies that the concentration quenching mechanism in Ce\(^{3+}\) emission is strongly accounted for by the dipole–dipole interaction. With increasing Ce\(^{3+}\) concentration, the wavelengths of excitation and emission bands remain practically unchanged for the phosphor material. In addition, the optical absorbance (\(\phi\)) and quantum efficiency (\(\eta\)) were calculated by using the following equations:

\[
\phi = \frac{L_n(\lambda) - L(\lambda)}{L(\lambda)}
\]

\[
\eta = \frac{L(\lambda)}{I(\lambda)}
\]

Figure 4. (a) PLE spectra (monitored at \(\lambda_{em} = 471\) nm) and (b) PL spectra (\(\lambda_{ex} = 410\) nm) of Ba(La\(_{1−x}\)Ce\(_x\))\(_2\)Si\(_2\)S\(_8\) with different Ce\(^{3+}\) concentration x. The inset shows the correlation between \(\log(I/x)\) with \(\log(x)\).
In spite of the introduction of Si ions, the density of phonons, and the probability of increasing temperature increases the population of higher vibration levels, the nonradiative transfer.44 In addition, for application in higher-powered LEDs, chemical stability of a phosphor is an important parameter to consider. Figure S2 in the SI presents the time-dependent PL intensity of Ba(La0.94Ce0.06)2Si2S8 exposed to ambient air. The PL intensity drops only ~25% when exposed to ambient air for 5 weeks. This observation can illustrate that the BaLa2Si2S8:Ce3+ thiosilicate phosphor is mostly stable against degradation in ambient condition.

Furthermore, the decay curves of Ba(La1−xCe)x2Si2S8 (x = 0.01, 0.06, and 0.10) phosphors excited at 420 nm and monitored at 471 nm are shown in Figure 6 and Figure S3 in the SI. The corresponding luminescence decay lifetime value can be calculated to be 34.93, 32.33, and 30.41 ns, using the first-order exponential equation.45

\[ I = I_0 \exp\left(-\frac{t}{\tau}\right) \]  

where \( I \) and \( I_0 \) are the luminescence intensities at time \( t \) and 0, respectively, and \( \tau \) is the decay lifetime. The lifetime of Ce3+ in Ba(La1−xCe)x2Si2S8 is in the range of nanosecond, which is also reasonable for the 5d−4f transitions of Ce3+46 and similar to that usually observed47−49 (see Table S1 in SI). With increasing Ce3+ concentration, both the energy transfer rate between Ce3+−Ce3+ and the probability of energy transfer to quenching sites increase and, as a result, the lifetime shortened with the increasing Ce3+ concentration. However, due to the longer La−La distance (∼5.5 Å) in Ba(La1−xCe)x2Si2S8, the low energy transfer rate between Ce3+ may result and, thus, a large change in the lifetime with variation of the Ce3+ concentration was not observed in Ba(La1−xCe)x2Si2S8.44 Moreover, the well-fitting results by exponential decay with a single component illustrate that Ce3+ ions occupy only one site in the BaLa2Si2S8 host, which is consistent with the Rietveld refinement of BaLa2Si2S8:Ce3+ and the PL spectra shown in Table 1 and Figure 4b, respectively.

Figure 5. Temperature-dependent PL intensity of Ba(La0.99Ce0.01)2Si2S8 and Ba(La0.94Ce0.06)2Si2S8. The inset shows the fitted PL intensity and the calculated thermal activation energy (\( \Delta E \)) as a function of temperature.

Figure 6. Decay curve for Ba(La0.99Ce0.01)2Si2S8 phosphor (black line) and curve-fitting (red line) under 420 nm excitation and monitored at 471 nm.
CIE Chromaticity Coordinates and Performance of LED Device Based on Ba(La0.94Ce0.06)2Si2S8 Phosphor. To demonstrate the potential of Ba(La1−xCex)2Si2S8 for pc-WLEDs application, the Ba(La0.94Ce0.06)2Si2S8 phosphor was utilized to fabricate a white LED device driven by 350 mA current with red-emitting CaAlSiN3:Eu2+ phosphor and a 430 nm InGaN-based LED chip, as illustrated in Figure 7a. The whole visible spectral region can be obtained when excited by the blue chip, and the color rendering index (Ra) of this trichromatic pc-WLED was determined to be around 72. The Commission International de l’Eclairage (CIE) chromaticity coordinates and the correlated color temperature (CCT) of the pc-WLED were measured as \((x, y) = (0.312, 0.304)\) and 5981 K and shown in Figure 8. With the addition of proprietary yellow-emitting (Sr, Ca)2SiO4:Eu2+ phosphor, the CRI value could be improved to 96, as illustrated in Figure 7b. The corresponding CIE chromaticity coordinates and CCT were measured to be \((x, y) = (0.332, 0.329)\) and 5385 K, respectively. In fact, the main drawback of thiosilicate phosphors is the downgrade for high-temperature long-term operation. However, the pc-WLEDs performance can still be further ameliorated by more precise device construction, such as thermal module.

**CONCLUSION**

We have investigated and reported the synthesis, crystal structure, and luminescence of a unprecedented Ce3+-activated thiosilicate phosphor with chemical compositions of Ba(La1−xCex)2Si2S8 (x = 0.01, 0.02, 0.04, 0.06, 0.08, and 0.10). The overall luminescence performances (i.e., PL/PLE intensity, QE), decay lifetime, thermal-quenching behavior, and its application in LED fabrication were investigated. The detailed crystal structure, the morphology, and the EDS spectrum were also presented. The results show that this novel cyan-emitting phosphor can be excited over a broad range from UV to blue light and generate broadband emission. By integrating the Ba(La0.94Ce0.06)2Si2S8 yellow- and red-emitting phosphors on blue chip, we can obtain a warm-white-light LED device with high CRI value of 96 and CCT value of 5385 K. Our investigation results indicate that this material can potentially serve as conversion phosphors for pc-LEDs.

**ASSOCIATED CONTENT**

* Supporting Information
Further details are given in Figure S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*E-mail: tmchen@mail.nctu.edu.tw.

**Notes**
The authors declare no competing financial interest.

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**REFERENCES**


