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# Luminescent Supramolecular Microstructures Containing Ru(bpy)<sub>3</sub><sup>2+</sup>: Solution-Based Self-Assembly Preparation and Solid-State Electrochemiluminescence Detection Application

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In this correspondence, we report on the first preparation of novel, robust Ru(bpy)<sub>3</sub><sup>2+</sup>-containing supramolecular microstructures via a solution-based self-assembly strategy, carried out by directly mixing H<sub>2</sub>PtCl<sub>6</sub> and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> aqueous solutions at room temperature. It reveals that both the molar ratio and concentration of reactants have a heavy influence on the morphologies of such microstructures. The electrochemical behavior of the Ru(bpy)<sub>3</sub><sup>2+</sup> components contained in the solid film of the microstructures formed on the electrode surface is also studied and found to exhibit a diffusion-controlled voltammetric feature. Most importantly, such microstructures exhibit excellent electrochemiluminescence (ECL) behaviors and therefore hold great promise as new luminescent materials for solid-state ECL detection in capillary electrophoresis (CE) or CE microchip.

Electrochemiluminescence (ECL), the production of light from electrochemically generated reagents,<sup>1</sup> has been paid considerable attention during the past several decades due to its versatility, simplified optical setup, very low background signal, and good temporal and spatial control and has become an important and valuable detection method in analytical chemistry over the past years.<sup>2</sup> ECL has found many applications, such as in immunoassays and DNA analyses,<sup>3</sup> chemical sensing,<sup>4,5</sup> imaging,<sup>6,7</sup> lasing,<sup>8</sup> and optical studies,<sup>9</sup> and has been also used as detectors for chromatography<sup>10</sup> and capillary electrophoresis.<sup>11</sup> Ruthenium(II) tris(bipyridine) (Ru(bpy)<sub>3</sub><sup>2+</sup>) is one of the most extensively studied

and used ECL compounds due to its superior properties including high sensitivity and high stability under moderate conditions in aqueous solution.<sup>12</sup>

Self-assembly refers to the spontaneous organization of molecules, molecular clusters, and aggregate structures into two-dimensional (2D) arrays and three-dimensional (3D) networks by attractive forces or chemical bond formation. It provides an effective and versatile approach for constructing a structured system at a molecular level.<sup>13</sup> Among them, the most often studied involves self-assembled monolayers formed on planar solid substrates,<sup>14</sup> monolayer-protected clusters,<sup>15</sup> self-assembly into 3D networks on planar solid substrates,<sup>16</sup> layer-by-layer self-assembly of ultrathin films on planar solid substrates<sup>17</sup> or colloidal particles,<sup>18</sup> etc. On the other hand, solution-based self-assembly has also been paid increasing attention because it provides a means for the integration of molecular systems into functional mesoscopic devices and macroscopic materials.<sup>19</sup> In this correspondence, we report on, to the best of our knowledge, the first preparation of novel, robust Ru(bpy)<sub>3</sub><sup>2+</sup>-containing supramolecular microstructures via a solution-based self-assembly strategy, carried out by directly mixing H<sub>2</sub>PtCl<sub>6</sub> and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> aqueous solutions at room temperature. It is found that both the molar ratio and concentration of reactants have heavy influence on the morphologies of such microstructures and the electroactive Ru(bpy)<sub>3</sub><sup>2+</sup> components contained in the solid film of such microstructures formed on the electrode surface exhibit a diffusion-controlled voltammetric feature. Most importantly, such microstructures exhibit excellent ECL behaviors and therefore hold great promise as new functional materials for solid-state ECL detection in capillary electrophoresis (CE) or CE microchip.

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## EXPERIMENTAL SECTION

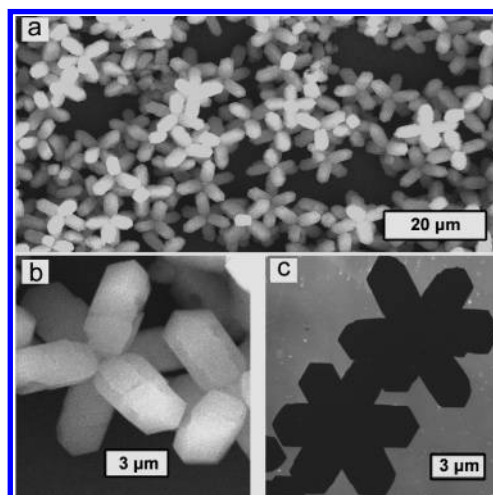
$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_2\text{PtCl}_6$  were purchased from Aldrich. All reagents were used as received without further purification. The water used was purified through a Millipore system. Sample 1 was prepared as follows: In a typical experiment, 80  $\mu\text{L}$  of 0.038 M  $\text{H}_2\text{PtCl}_6$  aqueous solution was introduced into 3 mL of water first, and then 61  $\mu\text{L}$  of 0.05 M  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  aqueous solution (1:1 molar ratio of Ru to Pt) was added into the resulting solution under vigorous stirring (so that these two components can be mixed uniformly) at room temperature. After the addition was completed, stirring was stopped and the resulting solution was kept at room temperature. Several minutes later, the formation of a large amount of precipitate occurred. The resulting precipitate was collected by centrifugation, washed several times with water, and then suspended in water. The suspension thus formed was used for further characterization.

For characterization by scanning electron microscopy (SEM), 100  $\mu\text{L}$  of the suspension was placed on an indium tin oxide (ITO) glass slide and air-dried at room temperature. SEM measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. A sample for TEM characterization was prepared by placing a drop of the suspension on a carbon-coated copper grid and drying at room temperature. UV-vis spectra were collected on a Cary 500 Scan UV-vis-near-infrared (UV-vis-NIR) spectrophotometer. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation. A sample for XRD characterization was prepared by placing 100  $\mu\text{L}$  of the suspension on a glass slide. The electrode for electrochemical and ECL analysis was fabricated by placing 10  $\mu\text{L}$  of the suspension on an ITO glass electrode and air-dried at room temperature. A model 800 electrochemical analyzer (CHI Instruments, Co., Austin, TX) was used to perform cyclic voltammetry. ECL signals were monitored by a MCFLA multifunctional chemiluminescent and bioluminescent analytical system (Remax Electronic Co., Ltd.) with the voltage of the photomultiplier tube set at 800 V.

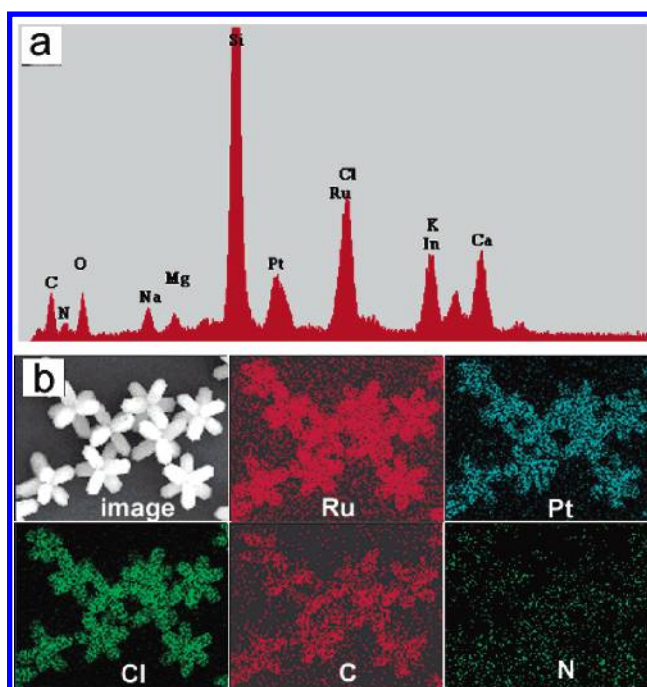
## RESULTS AND DISCUSSION

Figure 1 shows typical SEM and TEM images of the resulting precipitate of sample 1. Figure 1a shows a low-magnification SEM image. It is clearly seen that the precipitate consists of a large quantity of star-shaped microstructures with six branches. A higher magnification SEM image as shown in Figure 1b reveals that each branch has identical length and its surface is smooth, which can be further confirmed by the corresponding TEM image as shown in Figure 1c. It is worthwhile mentioning that the structures thus formed are robust enough to stand a violent sonication process. To investigate the time-dependent morphology evolution of such microstructures, we collected SEM images with elapsed times of about 2, 5, and 10 min after the mixing of  $\text{H}_2\text{PtCl}_6$  and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  aqueous solutions (Supporting Information Figure S1). It should be noted that each sample gives quite similar structures to the final products, indicating that the formation of such star-shaped microstructures is a fast process.

The chemical composition of the resulting microstructures was determined by energy-dispersed spectrum (EDS) and X-ray maps



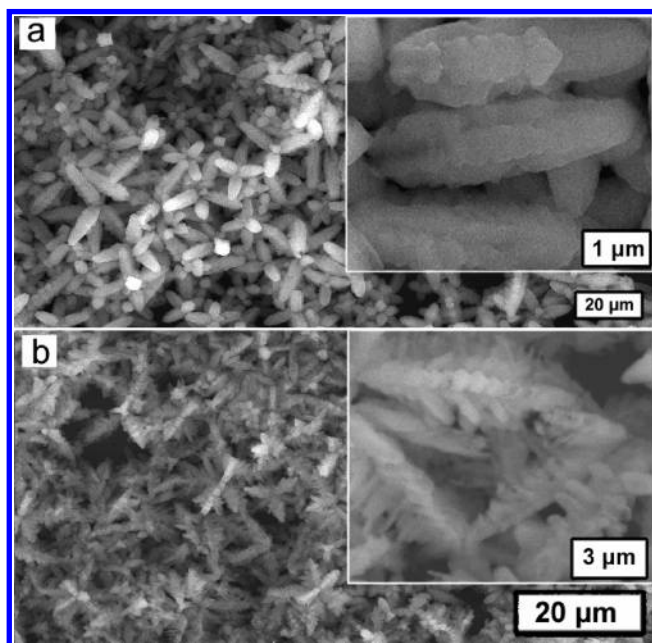
**Figure 1.** (a) Low-magnification SEM, (b) high-magnification SEM, and (c) TEM image of the resulting precipitate of sample 1.



**Figure 2.** (a) EDS and (b) X-ray maps of the precipitate of sample 1.

analysis of the products coated on an ITO glass slide (Figure 2). The EDS spectrum (Figure 2a) shows peaks corresponding to Ru, Pt, Cl, C, and N elements (other peaks originated from the substrate). The corresponding X-ray maps (Figure 2b) reveal that these five elements are relatively uniform distributed in these microstructures. Based on these observations, we can conclude that these structures are products formed from  $\text{PtCl}_6^{2-}$  and  $\text{Ru}(\text{bpy})_3^{2+}$ . Considering the positive charge of  $\text{Ru}(\text{bpy})_3^{2+}$  and the negative charge of  $\text{PtCl}_6^{2-}$ , we may suggest that electrostatic attractions between these two complexes drive the formation of micrometer-scale supramolecular microstructures. We also did another control experiment by mixing  $\text{Ru}(\text{bpy})_3^{2+}$  and other negatively charged metal salts such as  $\text{HAuCl}_4$  and  $\text{H}_2\text{PdCl}_4$  and obtained microstructures (Supporting Information Figure S2). Please note that the mix of  $\text{Ru}(\text{bpy})_3^{2+}$  with other metal cations such as  $\text{Cu}^{2+}$  ions only gave a clear solution, not a precipitate, which may be attributed to the fact that there are only electrostatic





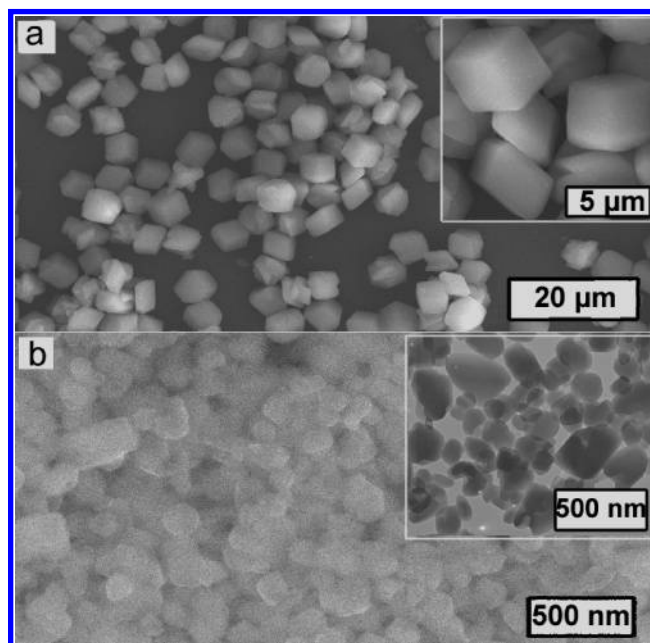
**Figure 3.** Low and high (inset) magnification SEM images of the precipitate obtained with Ru/Pt molar ratio (a) 2:1 and (b) 4:1, under otherwise identical conditions used for preparing sample 1.

repulsions between positively charged  $\text{Ru}(\text{bpy})_3^{2+}$  and positively charged  $\text{Cu}^{2+}$ , which prevent these two components from forming larger aggregated structures.

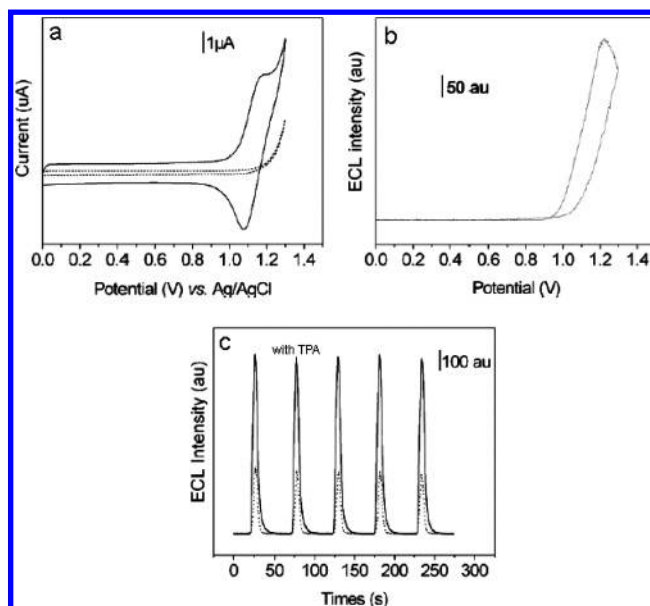
We collected the UV-vis absorption spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  aqueous solution and the microstructures suspension in water (Supporting Information Figure S3) and found that the spectra of the microstructures suspension in water is quite similar to that of  $\text{Ru}(\text{bpy})_3^{2+}$  aqueous solution, further indicating that only pure electrostatic interactions are responsible for the formation of the microstructures. To determine the stoichiometry, we performed quantitative elemental analysis and found that the atom number ratio of C/N/Ru/Pt/Cl in as-formed microstructures is 29.9:6:1:1.02:6, revealing that the  $\text{Ru}(\text{bpy})_3^{2+}/\text{PtCl}_6^{2-}$  stoichiometry is 1:1, which is quite consistent with the 1:1 reaction molar ratio of Ru to Pt. We also collected the XRD patterns of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ ,  $\text{H}_2\text{PtCl}_6$ , and the microstructures (Supporting Information Figure S4). The pattern of the microstructures shows several peaks and the strongest peak occurs at  $7.9^\circ$ . Clearly, compared with  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  or  $\text{H}_2\text{PtCl}_6$ , the microstructures exhibits a quite different XRD pattern and the crystal nature of the microstructures is quite different from the two components. However, owing to lack of standard or referenced XRD data on this kind of new structures, at present we cannot provide detailed information on the crystal nature of the microstructures obtained.

We examined the effect of the molar ratio of reactants on the microstructures obtained by preparing another two samples at different Ru/Pt molar ratio, under otherwise identical conditions used for preparing sample 1. When the molar ratio is increased to 2:1, we obtain corn cob-like microstructures with relatively rough surface and find that these microstructures exist in isolated or star-shaped forms, as shown in Figure 3a. When the molar ratio is further increased to 4:1, we obtain palm leaf-like microstructures that also exist in isolated or star-shaped forms, as shown in Figure 3b.

We further investigate the effect of concentration of reactants on the microstructures. Figure 4 shows typical SEM images of

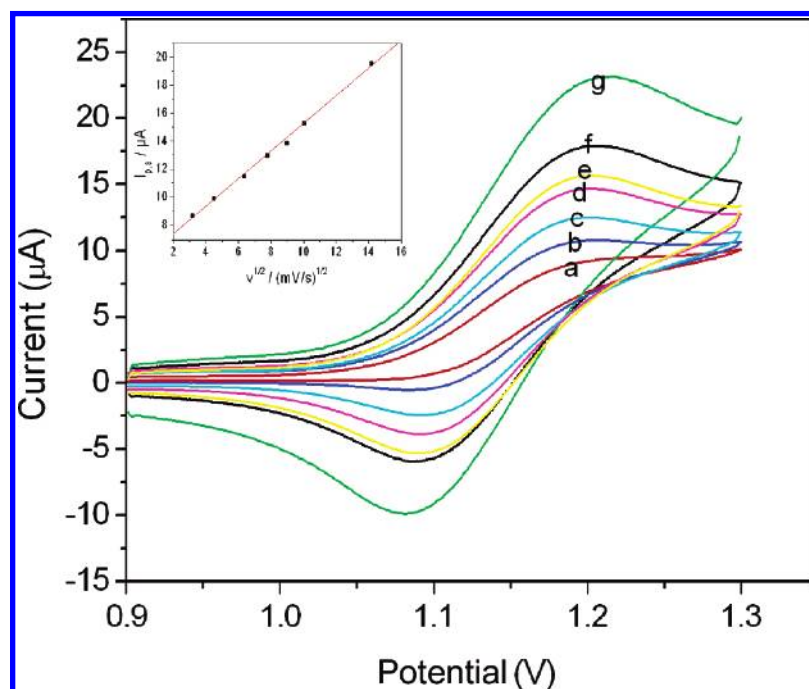


**Figure 4.** SEM images of the precipitate obtained at (a) one-fifth and (b) 5-fold the concentration of reactants, under otherwise identical conditions used for preparing sample 1. (Inset in a shows corresponding enlarged SEM image, and inset in b shows corresponding TEM image.)



**Figure 5.** (a) CVs of bare (dashed line) and microstructure-coated (solid line) ITO electrode at scan rate of 50 mV/s. (b) ECL intensity-potential curve of microstructure-coated ITO electrode in 50 mM phosphate buffer solution (pH 9.2). (c) ECL intensity-time curve of microstructure-coated ITO electrode in 50 mM phosphate buffer solution (pH 9.2) in the absence (dot line) and presence (solid line) of 25  $\mu\text{M}$  TPA under continuous CVs for 5 cycles.

another two samples obtained at different concentrations of reactants, under otherwise identical conditions used for preparing sample 1. When the concentration of both  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and  $\text{H}_2\text{PtCl}_6$  is decreased to one-fifth, it is found that the resulting precipitate consists of particles with cubic and irregular morphologies, as shown in Figure 4a. However, when the concentration of both  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and  $\text{H}_2\text{PtCl}_6$  is increased 5-fold, the precipitate consists



**Figure 6.** CVs of the microstructures on an ITO electrode in 50 mM phosphate buffer solution (pH 9.2) at different scan rates: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, and (g) 200 mV/s. Inset: the relationship between the anodic peak current and the square root of the scan rate.

of irregular particles with drastically broad size distribution and the particle size decreases drastically, as shown in Figure 4b.

To test the ECL behaviors of as-prepared supramolecular microstructures, we acquired the CVs, ECL intensity–potential curve, and ECL intensity–time curve of the microstructures of sample 1 coated on an ITO glass electrode. Figure 5a shows the CVs of bare (dashed line) and microstructure-coated (solid line) samples at a scan rate 50 mV/s in 50 mM phosphate buffer solution (pH 9.2). A pair of redox wave appears at  $\sim 1.1$  V (vs Ag/AgCl), which is attributed to the one-electron redox reaction of  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>20</sup> Figure 5b shows corresponding the ECL intensity–potential curve of the microstructure-coated ITO glass electrode. The onset of luminescence occurs near 0.9–1.0 V, which is consistent with the oxidation of the  $\text{Ru}(\text{bpy})_3^{2+}$ ,<sup>21</sup> and then the ECL intensity arises steeply. Figure 5c shows the ECL intensity–time curve in phosphate buffer solution (pH 9.2) in the absence (dot line) and presence (solid line) of 25  $\mu\text{M}$  tripropylamine (TPA) under continuous potential scanning for five cycles. The relative standard deviation is 0.6%. Based on the following two observations, (1) these microstructures are robust enough to stand violent sonication process; (2) when the ITO electrode coated with such microstructures is replaced with a bare ITO electrode, the redox waves characteristic of  $\text{Ru}(\text{bpy})_3^{2+}$  and corresponding ECL signals disappear, it is reasonable to conclude that no  $\text{Ru}(\text{bpy})_3^{2+}$  contained in these microstructures is dissolved into the solution. Therefore, we can suggest that the CVs and corresponding ECL signals observed can be attributed to  $\text{Ru}(\text{bpy})_3^{2+}$  components contained in the microstructures on the electrode surface. These observations suggest that the microstructures thus formed exhibit excellent ECL behaviors and therefore hold great promise for solid-state ECL detection in CE or CE microchip. Note that the

other samples also exhibit good ECL behavior (Supporting Information Figure S5).

Figure 6 shows the CVs of the microstructures of sample 1 coated on an ITO electrode in 50 mM phosphate buffer solution (pH 9.2) at different scan rates. The difference between the anodic and cathodic peak potential ( $\Delta E_p$ ) was 110 mV. Moreover, it was found that the peak current was proportional to the square root of scan rate  $v^{1/2}$  (inset) in the range of 10–500 mV/s, indicating that the  $\text{Ru}(\text{bpy})_3^{2+}$  components contained in the microstructures on the electrode surface underwent a diffusion-controlled process within the film.<sup>22</sup> Shankaran and Narayanan prepared a copper hexacyanoferrate precipitate, an ion conductor with redox active sites, by mixing  $\text{Cu}(\text{NO}_3)_2$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  aqueous solutions, and found that  $\text{Fe}(\text{CN})_6^{4-}$  components contained in the crystalline powder of the resulting precipitate immobilized on the electrode surface underwent a diffusing-controlled redox reaction.<sup>23</sup> In our present study, the crystalline microstructures were similarly prepared by mixing  $\text{H}_2\text{PtCl}_6$  and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  aqueous solutions, and therefore, it may be expected that the resulting hybrid material is an ion conductor with redox-active sites. As a result, it is reasonable that a diffusion-controlled voltammetric wave is observed for electroactive  $\text{Ru}(\text{bpy})_3^{2+}$  components contained in the solid film on the electrode surface.

In conclusion, novel  $\text{Ru}(\text{bpy})_3^{2+}$ -containing supramolecular microstructures with interesting morphologies have been prepared by directly mixing  $\text{H}_2\text{PtCl}_6$  and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  aqueous solutions at room temperature. It reveals that both the molar ratio and concentration of reactants have heavy influence on the morphologies of such microstructures and the electroactive  $\text{Ru}(\text{bpy})_3^{2+}$  components contained in the solid film of such microstructures formed on the

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electrode surface exhibit a diffusion-controlled voltammetric feature. Most importantly, such microstructures exhibit excellent ECL behaviors and therefore hold great promise as new luminescent materials for solid-state ECL detection in CE or a CE microchip.

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#### **SUPPORTING INFORMATION AVAILABLE**

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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