

# Facile Assembly Enhanced Spontaneous Fluorescent Response of Ag<sup>+</sup> Ion Containing Polyelectrolyte Multilayer Films

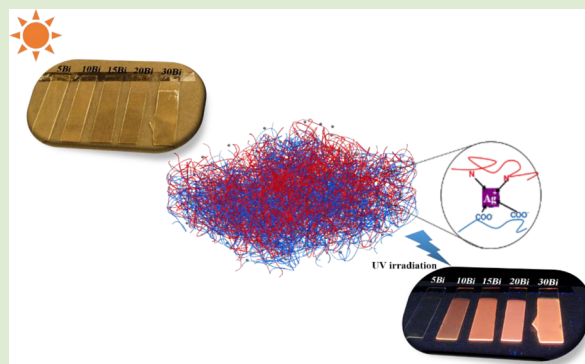
Xiayun Huang<sup>†</sup> and Nicole S. Zacharia<sup>\*,†,‡</sup>

<sup>†</sup>Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States

<sup>‡</sup>Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325, United States

## S Supporting Information

**ABSTRACT:** Fluorescent organic–inorganic composite materials exhibiting “turn-on” response are often based on conjugated small molecules. Conjugated polymers, however, often exhibit a “turn-off” response in combination with metal ions. Here we present fluorescent turn-on behavior of a branched poly(ethylene imine)-poly(acrylic acid)-Ag<sup>+</sup> ion complex in a thin film. The material is characterized by UV–vis, spectrofluorometry, XPS, and ICP-MS. The turn-on response is exhibited only with all three components present, implying that the optically active metal coordination complex contains amine and carboxylic acid groups. This behavior is observed in the solid state, meaning this material could be easily integrated into devices. We demonstrate sensing of formaldehyde vapor as well as halide containing solutions based on fluorescence quenching. This fluorescent material is simply made using the layer-by-layer technique and commercially available polymers.



Coordinative assembly, taking advantage of coordination complex formation, allows organic–inorganic functional assemblies to be formed from combinations of polymers, oligomers, metal ions, and metallopolymers.<sup>1–4</sup> Functionality of these materials includes optical properties such as fluorescence. Many fluorescent organo-metallic complexes are formed from the combination of a conjugated small molecule and a metal ion.<sup>5,6</sup> On the other hand, fluorescence of conjugated polyelectrolytes is often quenched (turn-off response) upon complexation with metal ions.<sup>7–9</sup> This can be explained by self-quenching and intermolecular energy transfer caused by the aggregation of chromophores in aqueous solution, or aggregation-caused quenching.<sup>10</sup>

In certain cases when nonluminescent organic gelators aggregate, their gelation actually enhances luminescent emission (turn-on response).<sup>11–13</sup> One example is organogels assembled through metal ion coordination complexes. However, there are only a few reports describing fluorescent Ag<sup>+</sup> ion complexes, usually with conjugated small molecules, and Ag<sup>+</sup> ion complexation induced formation of fluorescent supramolecular gels.<sup>14</sup> More commonly, quenching of photoluminescence occurs, even though the unbound ligand may exhibit a strong fluorescence before chelating with Ag<sup>+</sup> ion.<sup>14</sup> Therefore, creation of this turn-on type of fluorescent probe in combination with Ag<sup>+</sup> ion still remains a significant challenge. Park et al.<sup>11</sup> presented a turn-on fluorescent supramolecular gel triggered by coordination of silver ion with a conjugated small molecule. The ligand itself is nonfluorescent in solution but it then becomes highly fluorescent when self-assembled with Ag<sup>+</sup>

ion to form supramolecular fibers. Zhang et al.<sup>15,16</sup> reported a turn-on fluorescent gel based on tetraphenylethylene derivatives, which show very weak fluorescence in solution, but when complexed with Ag<sup>+</sup> ion, a strong emission is exhibited.

The layer-by-layer (LbL) method for directing the complexation of polyelectrolytes is a versatile tool for creating thin films called polyelectrolyte multilayers (PEMs) composed of a range of components, including metal ions.<sup>2</sup> This technique can be used with charged materials as well as hydrogen bonds and materials using other types of associations. Here we report a branched poly(ethylene imine)/poly(acrylic acid) (BPEI/PAA)-Ag<sup>+</sup> ion complex system deposited fabricated using the LbL method that exhibits a spontaneous fluorescence similar to the “turn-on” phenomena. The components in the system are nonconjugated polyelectrolytes, which are not fluorescent in the absence of silver ions. The complex containing film is prepared by sequential exposure of a substrate to solutions of BPEI and PAA until the desired number of layers is achieved. Ag<sup>+</sup> ion is introduced into the assembly by a stable polyelectrolyte-ion complex with either BPEI or PAA being formed in solution which is then used for film assembly, an approach similar to that used by Bruening et al. to introduce palladium into PEMs.<sup>17,18</sup> During assembly, Ag<sup>+</sup> ion is incorporated into the multilayer through chelation with both amine groups of BPEI and carboxylic acid groups of PAA. The

Received: August 31, 2014

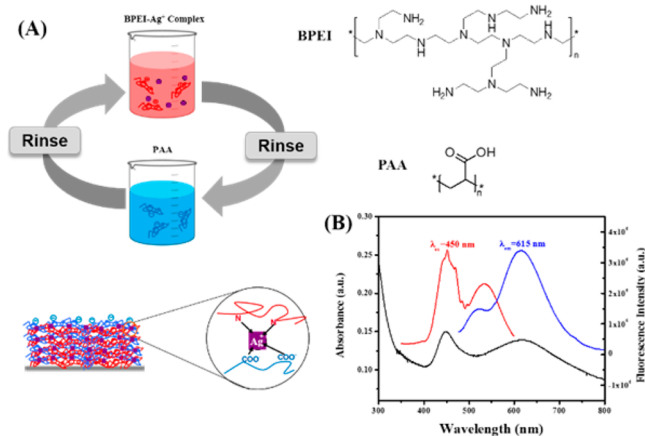
Accepted: October 7, 2014

Published: October 9, 2014

PEM in the absence of  $\text{Ag}^+$  is nonfluorescent, as are complexes containing a single polyelectrolyte and  $\text{Ag}^+$  ion. Once  $\text{Ag}^+$  ions are included in the assembly process, no matter if first complexed with BPEI or PAA, an orange emission is generated under UV irradiation. If silver ion is incorporated in both solutions, fluorescence is also observed in the film. This phenomenon is caused by the  $\text{Ag}^+$  ion forming a complex with both BPEI and PAA to form a supramolecular structure and then the consequent splitting of HOMO and LUMO levels with an energy difference that matches the photoluminescence emission.

To reiterate, the phenomena is seen both when  $\text{Ag}^+$  ion is complexed first with BPEI or with PAA. If a pristine (no metal ion) BPEI/PAA multilayer is exposed to  $\text{Ag}^+$  ion solution, after some time it will also show this response, in true “turn-on” fashion. However, these films also become rough and scatter so quantitative measurement of the fluorescence is difficult. Additionally, fluorescence is not seen when other polycations such as linear poly(ethylene imine), which contains only secondary amines, and poly(allylamine hydrochloride), which contains only primary amines or polydimethyldially ammonium chloride, containing quaternary amines, are used, but is also observed when polyamidoamine (PAMAM, G3- $\text{NH}_2$  surface) is used as the polycation. We believe this shows that linear polymers do not have the necessary geometry to form a fluorescent complex, as we have previously shown that BPEI can complex greater amounts of silver ion than linear polyamines, and perhaps the specific chemistry of the amines is important.

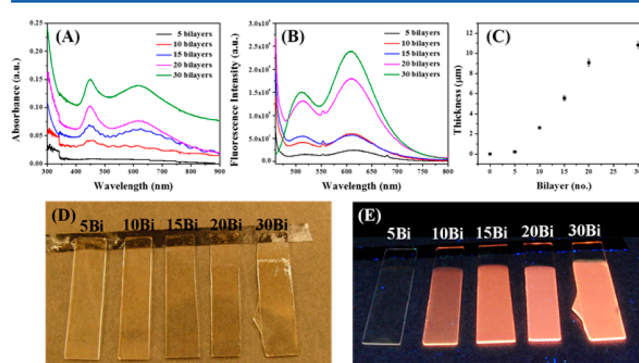
This PEM system, BPEI-metal ion/PAA, has been reported to have the ability to incorporate various transition metal ions, such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ag}^+$ , through both chelation with amine and carboxylic acid groups.<sup>2</sup> Here, PEMs were assembled using a BPEI- $\text{Ag}^+$  ion complex and PAA (Figure 1A). Deposition begins with a stable BPEI- $\text{Ag}^+$  ion complex with an excess of positive charges, which then complexes with negatively charged PAA in the subsequent deposition step. The



**Figure 1.** (a) Schematic representation of the multilayer assembly of BPEI- $\text{Ag}^+$ /PAA.  $\text{Ag}^+$  ions chelate with the amine groups of BPEI and the carboxylic acid groups of PAA (b) UV-vis (black) and fluorescence spectra of 30 bilayer BPEI- $\text{Ag}^+$ /PAA films. Red and blue spectra are the excitation (with fixed emission wavelength of 615 nm) and emission spectrum (with fixed excitation wavelength of 450 nm), respectively. Solution concentrations of BPEI and PAA were 40 and 20 mmol/L with respect to the repeat unit. Concentration of  $\text{Ag}^+$  ion in the BPEI- $\text{Ag}^+$  ion complex solution was 3 mmol/L.

$\text{Ag}^+$  ion is able to interact with both amine groups and carboxylic acid groups in the multilayer film as the polyelectrolytes assemble through metal–ligand interactions or electrostatics. The ion containing film is nearly colorless under visible light and emits an intense orange color under UV irradiation. The UV-vis spectrum (black) in Figure 1B shows the weak absorbance of the BPEI- $\text{Ag}^+$ /PAA film at 450 and 615 nm, matching the maximum fluorescence excitation (red spectrum) at 450 nm and the emission (blue spectrum) at 615 nm.

Similar to the growth of the BPEI/PAA system,<sup>19</sup> the BPEI- $\text{Ag}^+$ /PAA system grows superlinearly during the first 15 bilayers (i.e., successive layers deposit more thickly than previous ones)<sup>20</sup> following the “in” and “out” diffusion mechanism.<sup>21</sup> For films of this type, one (or both) of the polyelectrolytes are able to not only to add on to the surface of the LbL film but to diffuse into the bulk of the film. The film then grows linearly until  $\sim 10 \mu\text{m}$  in thickness (Figure 2C). Both UV-vis



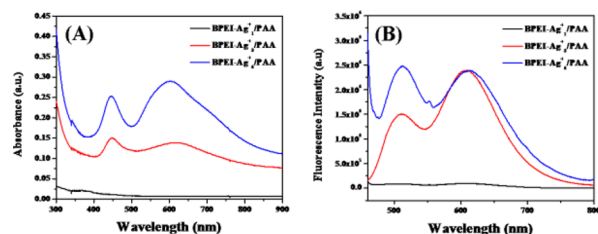
**Figure 2.** Growth of BPEI- $\text{Ag}^+$ /PAA film. UV-vis spectra (A), fluorescence spectra (B), and thickness (C) of BPEI- $\text{Ag}^+$ /PAA film with different bilayer number. The fluorescence spectra for films of different bilayer numbers were obtained using an excitation wavelength of 450 nm. Photographs of BPEI- $\text{Ag}^+$ /PAA film with different numbers of bilayers shown under visible light (D) and UV irradiation (E). Films are nearly colorless under visible light, while those under UV irradiation show an orange emission color and an increase in intensity with increasing bilayer number.

absorbance (Figure 2A) and fluorescence intensity (Figure 2B) increase with bilayer number, showing increasing incorporation of optically active complex. The peaks in these spectra do not shift during film growth. The relative intensity of the two emission peaks remains similar as the film grows. This means that the chelation mode in the film does not change distinguishably during growth. Although an increase in absorbance in the visible range can be detected, the film is nearly colorless to the eye under visible light (Figure 2D). Once these films are exposed to UV irradiation, light of an orange color is spontaneously emitted (Figure 2E).

To date, this is the first report of such a fluorescent “turn-on” phenomena using a PEM. Neither the BPEI- $\text{Ag}^+$  ion nor the PAA- $\text{Ag}^+$  ion solution exhibits fluorescence, which is seen only once the (BPEI/PAA)- $\text{Ag}^+$  multilayer is formed. The origin of the fluorescence in this is due to chelation of  $\text{Ag}^+$  ion with BPEI and PAA, not the formation of reduced Ag nanoclusters. It has been demonstrated that Ag clusters as part of a PEM can also generate fluorescence due to discontinuous band structures.<sup>22–25</sup> Photochemical reduction of the  $\text{Ag}^+$  ion within the film to form Ag nanoclusters, however, results in quenching of the fluorescence (Figure S1). This indicates that in this case the

source of the emission is the coordination complex, not Ag nanoclusters. The fluorescence emission at 615 nm is quenched via both thermal (Figure S2) and chemical reduction (Figure S3) of Ag. Also, different than the single emission band exhibited by Ag nanoclusters both in solution<sup>1,22–25</sup> and in films,<sup>26–28</sup> two overlapping emission bands at 515 and 615 nm are observed for the BPEI-Ag<sup>+</sup>/PAA film with an excitation at 450 nm. The presence of two peaks indicates multiple types of bonding between the two polyelectrolytes and the Ag<sup>+</sup> ion. Fluorescence is also observed in PAMAM/PAA-Ag<sup>+</sup> films, which includes all of these same functional groups as BPEI. In the PAMAM case two emission bands are observed but are much weaker compared with BPEI/PAA-Ag<sup>+</sup> films.

The UV-vis absorbance and fluorescence intensity may be varied by manipulation of Ag<sup>+</sup> ion concentration in solution. Even though the Ag<sup>+</sup> ion in either BPEI or PAA solution used for LbL assembly is not completely incorporated into the film (Table S1), an increase in Ag<sup>+</sup> ion concentration in the complex solution does increase the Ag<sup>+</sup> ion content in the film.<sup>2</sup> Solutions with different Ag<sup>+</sup> ion concentrations (1, 3, and 6 mmol/L) form complexes with BPEI that are stable as long as several weeks. When assembled into a film with PAA, both the UV-vis absorbance and the intensity of fluorescence of the films increase with the increase in Ag<sup>+</sup> ion concentration in BPEI-Ag<sup>+</sup> complex solution, shown in Figure 3A. Moreover, the



**Figure 3.** UV-vis (A) and fluorescence emission spectra (B) of 30 bilayer BPEI-Ag<sup>+</sup>/PAA films assembled with different Ag<sup>+</sup> concentrations in the BPEI-Ag<sup>+</sup> complex solution. Emission spectra were obtained with a 450 nm excitation and their relative intensities increase as the Ag<sup>+</sup> ion concentration increases from 1 to 6 mmol/L. The concentration of BPEI and PAA were 40 and 20 mmol/L with respect to the repeating group. The concentration of Ag<sup>+</sup> ion in the BPEI-Ag<sup>+</sup> ion complex solution was 1, 3, and 6 mmol/L in the BPEI-Ag<sup>+</sup> ion complex solution for LbL assembly.

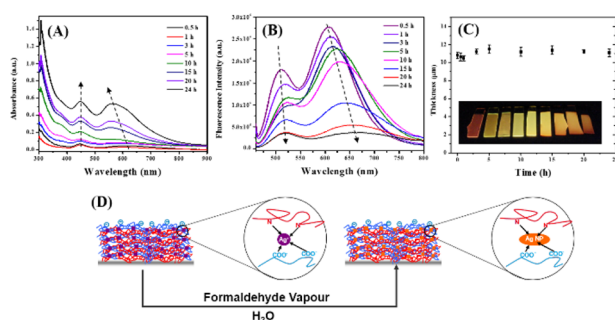
ratio of emission intensity of the peak at 515 nm to the peak at 615 nm increases when the Ag<sup>+</sup> ion concentration was 6 mmol/L in solution as compared to the films made with lower silver ion concentrations. The emission intensity at 615 nm is unchanged for the 3 and 6 mmol/L cases, while the emission intensity at 515 nm increases when changing from 3 to 6 mmol of Ag<sup>+</sup> ion in the assembly solution, seen in Figure 3B. In the UV-vis spectrum, an increase in the band at 615 nm when the Ag<sup>+</sup> ion concentration increases to 6 mmol/L was also observed. The changes in relative intensity of these two peaks may be indicative of the types of metal-ligand interactions changing, or their relative ratios changing in the films with increasing Ag<sup>+</sup> ion content. The two emission bands at 515 and 615 nm in the fluorescence spectra are always at the same wavelength but different intensities depending on assembly conditions. These conditions include Ag<sup>+</sup> ion concentration, molecular weight of polyelectrolytes, and by introducing silver in different assembly solutions (Figure S4). Molecular weight can influence emission intensity even when the polymer in

question is not the one complexed with Ag<sup>+</sup> ion in assembly solution.

In order to study the chelation mode in the film, ATR-FTIR and XPS were chosen to investigate both the metal-ligand interactions in the film and the amount of Ag<sup>+</sup> ion in the film. The ATR-FTIR spectra of the BPEI-Ag<sup>+</sup>/PAA film (Figure S5) does not show any distinguishable shifts in the peaks with increasing Ag<sup>+</sup> ion concentration during assembly. Most (~85%) of the carboxylate groups of PAA are deprotonated and form either metal-ligand coordination complexes with Ag<sup>+</sup> ion or electrostatic interactions with BPEI, while the amine groups exist in both protonated and deprotonated states (Figure S6). The amount of Ag<sup>+</sup> ion incorporated into the film is influenced by such factors as the charge densities of the polyelectrolyte complexes and the strength of the metal-ligand coordination complexes. PAA is less able to form a stable complex with Ag<sup>+</sup> ion at higher silver ion concentrations. The complex starts to precipitate at an early stage, under the condition of Ag<sup>+</sup> ion concentration of 3 mmol/L and carboxylic acid group concentration of 20 mmol/L, at pH 4.5. However, BPEI can form a stable complex over a greater range of silver ion concentrations. BPEI is stable at conditions of Ag<sup>+</sup> ion concentration of 6 mmol/L and amine group concentration of 20 mmol/L, at pH 9.5. Even when the Ag<sup>+</sup> ion concentration (either in complex with BPEI or PAA) is fixed as 1 mmol/L, the charge density, affinity to Ag<sup>+</sup> and complex structure will have the distinguishable difference for the Ag<sup>+</sup> ion chelated with BPEI and PAA. Using a PAA-Ag<sup>+</sup> ion complex (as opposed to BPEI-Ag<sup>+</sup> ion complex) incorporates more Ag<sup>+</sup> into the film and has a higher intensity emission than BPEI-Ag<sup>+</sup> ion complex (Figure S4).

Formaldehyde is widely used in the manufacture of resins and construction materials. However, it is a toxic and allergenic chemical and accumulates widely over cities.<sup>29,30</sup> While there are numerous methods for detecting gaseous formaldehyde, there remains a need for an inexpensive and rapid technique. Our fluorescent film can be used as a simple method for formaldehyde detection. Formaldehyde is known to be a weak reducer for Ag<sup>+</sup> ion as Tollen's reagent. It can reduce Ag<sup>+</sup> ion to Ag nanoparticles in the presence of water.<sup>31,32</sup> Once met with formaldehyde vapor from an aqueous formaldehyde solution, the fluorescence of the film begins to be quenched (Figure 4B) and the film becomes brown in color (Figure 4A), representing the formation of nanoparticles. Silver nanoparticles are formed gradually with increasing exposure to formaldehyde vapor, which reduces the silver ions but does not change the film thickness (Figure 4C). This indirectly shows that it is the presence of Ag<sup>+</sup> ion, and not Ag nanoclusters, in the film which generates the emission. Additionally, detection of cyanide and halides in solution by quenching of fluorescence is also possible (Figure S7).

In summary, the (BPEI/PAA)-Ag<sup>+</sup> LbL system shows fluorescent "turn-on" phenomena, something rarely reported for metal ions complexed with nonconjugated polymers. The complex containing film was prepared via LbL assembly by sequential dipping in solutions of BPEI and PAA complexes with Ag<sup>+</sup>. A strong orange emission color is generated from the film with Ag<sup>+</sup>, but not from the BPEI-Ag<sup>+</sup> and PAA-Ag<sup>+</sup> ion complexes. The emission intensity can be tuned by Ag<sup>+</sup> ion concentration, which Ag<sup>+</sup> ion complex is used (that is, whether the silver ion is complexed first with the polyanion or the polycation), and the molecular weight of polyelectrolyte. The



**Figure 4.** UV-vis spectra (A), fluorescence spectra (B), and thickness of 30 bilayer BPEI-Ag<sup>+</sup>/PAA PEM film with exposure to formaldehyde vapor for different time. These are emission spectra for excitation at 450 nm. The concentration of BPEI and PAA were 40 mmol/L and 20 mmol/L with respect to the repeating group. The concentration of Ag<sup>+</sup> ion in the BPEI-Ag<sup>+</sup> ion complex solution was fixed as 3 mmol/L. The fluorescence quenches and the visible absorbance from 400 to 700 nm increases with increasing exposure to the formaldehyde vapor. Film thickness remains constant over this process. The photograph in (C) shows the fluorescence emission color of PEMs exposed to formaldehyde from 0 h (left) to 24 h (right) excited by UV irradiation. (D) The illustration shows the way formaldehyde vapor interact with Ag<sup>+</sup> ion in the PEM and reduce them to Ag nanoparticles (NP) in the existence of moisture.

fluorescent film can be used as formaldehyde vapor detection via Ag<sup>+</sup> reduction.

## ■ ASSOCIATED CONTENT

### Supporting Information

Methods and materials section, as well more detailed information on the characterization of this system, including the quenching of fluorescence in the presence of halides. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [nzacharia@uakron.edu](mailto:nzacharia@uakron.edu).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank the American Association of Railroads, as well as student support through NSF under Award DMR-1255612. The authors also thank Dr. Karen L. Wooley for the use of her UV-vis and FTIR instruments.

## ■ REFERENCES

- (1) Decher, G.; Schlenoff, J. B. *Multilayer thin film: sequential assembly of nanocomposite materials*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2012.
- (2) Huang, X.; Schubert, A. B.; Chrisman, J. D.; Zacharia, N. S. *Langmuir* **2013**, *29*, 12959–12968.
- (3) Mentbayeva, A.; Ospanova, A.; Tashmuhambetova, Z.; Sokolova, V.; Sukhishvili, S. *Langmuir* **2012**, *28*, 11948–11955.
- (4) Han, F. S.; Hiuchi, M.; Kurth, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 2073–2081.
- (5) Ahn, H.; Kin, S. Y.; Kin, O.; Choi, I.; Lee, C. H.; Shim, J. H.; Park, M. J. *ACS Nano* **2013**, *7*, 6162–6169.
- (6) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868–5923.

(7) Andrew, S.; Swager, T. M. *J. Am. Chem. Soc.* **2007**, *129*, 16020–16028.

(8) Lv, J.; Ouyang, C.; Yin, X.; Zheng, H.; Zuo, Z.; Xu, J.; Liu, H.; Li, Y. *Macromol. Rapid Commun.* **2008**, *29*, 1588–1592.

(9) Jaeger, W.; Bohrisch, J.; Laschewsky, A. *Prog. Polym. Sci.* **2010**, *35*, 511–577.

(10) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361–5388.

(11) Seo, J.; Chung, J. W.; Cho, I.; Park, S. Y. *Soft Matter* **2012**, *8*, 7617–7622.

(12) Li, H.; Zhu, Y.; Zhang, J.; Chi, Z.; Chen, L.; Su, C. Y. *RSC Adv.* **2013**, *3*, 16340–16344.

(13) Zhao, Z.; Lam, J. W. Y.; Tang, B. Z. *Soft Matter* **2013**, *9*, 4564–4679.

(14) Zhang, J. F.; Zhou, Y.; Yoon, J.; Kim, J. S. *Chem. Soc. Rev.* **2011**, *40*, 3416–3429.

(15) Liu, L.; Zhang, G.; Xiang, J.; Zhang, D.; Zhu, D. *Org. Lett.* **2008**, *10*, 4581–4584.

(16) Liu, L.; Zhang, D.; Zhang, G.; Xiang, J.; Zhu, D. *Org. Lett.* **2008**, *10*, 2271–2274.

(17) Kidambi, S.; Dai, J.; Bruening, M. L. *J. Am. Chem. Soc.* **2004**, *126*, 2658–2659.

(18) Kidambi, S.; Bruening, M. L. *Chem. Mater.* **2005**, *17*, 301–307.

(19) Wang, X.; Liu, F.; Zheng, X.; Sun, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 11378–11381.

(20) Huang, X.; Bolen, M. J.; Zacharia, N. S. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10267–10273.

(21) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12531–12535.

(22) Diez, I.; Ras, R. H. A. *Nanoscale* **2011**, *3*, 1963–1970.

(23) Qu, F.; Li, N. B.; Luo, H. Q. *Langmuir* **2013**, *29*, 1199–1205.

(24) Qu, F.; Li, N. B.; Luo, H. Q. *J. Phys. Chem. C* **2013**, *117*, 3548–3555.

(25) Qu, F.; Li, N. B.; Luo, H. Q. *Anal. Chem.* **2012**, *84*, 10373–10379.

(26) Zhang, W.; Song, J.; Liao, W.; Guan, Y.; Zhang, Y.; Zhu, X. X. *J. Mater. Chem. C* **2013**, *1*, 2036–2043.

(27) Zhang, J.; Xu, S.; Kumacheva, E. *Adv. Mater.* **2005**, *17*, 2336–2340.

(28) Shao, C.; Yuan, B.; Wang, H.; Zhou, Q.; Li, Y.; Guan, Y.; Deng, Z. *J. Mater. Chem.* **2011**, *21*, 2863–2866.

(29) Leikauf, G. D. In *Environmental Toxicants: Human Exposures and Their Health Effects*, 3rd ed.; Lippmann, M., Ed.; Wiley: Hoboken, NJ, 2009.

(30) *WHO air quality guidelines for Europe*, 2nd ed.; World Health Organization: Copenhagen, 2000.

(31) Zhou, Y.; Li, M.; Su, B.; Lu, Q. *J. Mater. Chem.* **2009**, *19*, 3301–3306.

(32) Chou, K. S.; Lu, Y. C.; Lee, H. H. *Mater. Chem. Phys.* **2005**, *94*, 429–433.