ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

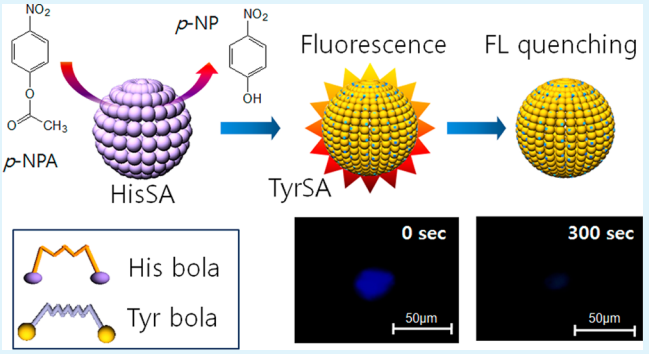
Biomimetic Catalytic and Sensing Cascades Built with Two Designer Bolaamphiphilic Self-Assemblies

Jinyoung Kwak,[†] Min-Chul Kim,[†] and Sang-Yup Lee*

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, Korea 120-749

Supporting Information

ABSTRACT: A system performing both a catalytic hydrolysis reaction and the direct optical monitoring of the product was created by the combination of two bolaamphiphile self-assemblies. Two bolaamphiphilic self-assemblies were applied as a biomimetic catalyst of *p*-nitrophenyl acetate (*p*-NPA) hydrolysis and an optical sensor probe that detects *p*-NPA hydrolysis through photoluminescence quenching by *p*-nitrophenol (*p*-NP), the product of *p*-NPA hydrolysis. One bolaamphiphilic self-assembly with a histidine moiety catalytically hydrolyzed the *p*-NPA substrate, and the other self-assembly of tyrosyl bolaamphiphile monitored the product of *p*-NP by photoluminescence quenching. The progression of the reaction and quenching degree were adjusted by controlling the quantity of histidyl and tyrosyl self-assemblies, respectively. The reaction and subsequent sensing cascade could be interrupted by a reducing agent. The addition of $NaBH_4$ induced the chemical conversion of *p*-NP to *p*-aminophenol, which retarded photoluminescence quenching. Thus, it was demonstrated that hydrolysis of an organic substrate and subsequent monitoring of the hydrolysis reaction could be achieved through a combination of independent bolaamphiphilic self-assemblies. This study demonstrated the construction of a catalytic reaction and detection system incorporating designer biomimetic self-assemblies whose functionalities were devised to realize deliberate functions.



KEYWORDS: *bolaamphiphile, self-assembly, hydrolysis, quenching, histidine, tyrosine*

INTRODUCTION

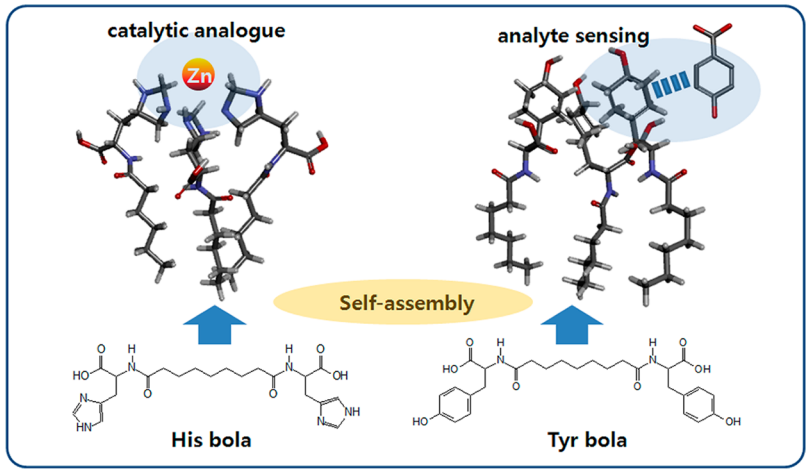
The bolaamphiphilic molecule, inspired by the lipid bilayer structure, has two hydrophilic groups at the ends of a central hydrophobic chain. Because of the hydrophobic−hydrophilic interaction, bolaamphiphilic molecules self-organize in an aqueous medium to create complex-structured assemblies with various chemical and physical properties.[1−3] One outstanding property of bolaamphiphilic self-assemblies over general surfactant micelles is their mechanical stability, which makes the self-assembled structures stable even under a vacuum and in a dried state. This outstanding mechanical stability permits the use of bolaamphiphilic self-assemblies as rigid templates or suprastructures for the synthesis of biomolecular, polymeric, and inorganic hybrid substances in controlled shapes.[4−6] In addition to their mechanical stability, bolaamphiphilic molecules with peptide hydrophilic moieties in particular offered unusual biochemical functionalities. Short peptides or amino acids have been applied as the biochemical hydrophilic groups upon synthesis of peptidic bolaamphiphilic molecules. The amino acids or peptides are densely arranged on the surface of the self-assemblies, which provides designer biochemical reactivity.[7−9] This biochemical reactivity with structural stability makes peptidic bolaamphiphilic self-assemblies promising for the creation of biomimetic substances whose reactivity can be manipulated by the design of conjugated peptides.[10−12]

The construction of a biomimetic system that simultaneously performs a biochemical reaction and detects the reaction's progress like a natural organism remains a challenge in biomimetics research. In particular, the creation of such a system by means of peptidic bolaamphiphilic self-assemblies has not been explored before. We recently reported on a CO_2 hydrating catalyst that was prepared from a histidyl bolaamphiphilic self-assembly (HisSA, Scheme 1a).[13] The histidyl bolaamphiphile self-organized to create a densely packed histidine imidazole array on the surface of the self-assembly. When surface-exposed histidine imidazole groups were exploited, catalytic analogues of a carbonic anhydrase were created by a coordinating Zn ion cofactor. At this catalytic analogue, hydrolysis of the substrate occurred. In addition, a tyrosyl bolaamphiphilic self-assembly (TyrSA, Scheme 1a) associated with photosensitizing substances was proven applicable as an optical sensor probe with photoluminescence.[14] The tyrosine phenol group enhanced photoluminescence through the antenna effect and was exploited as a binding

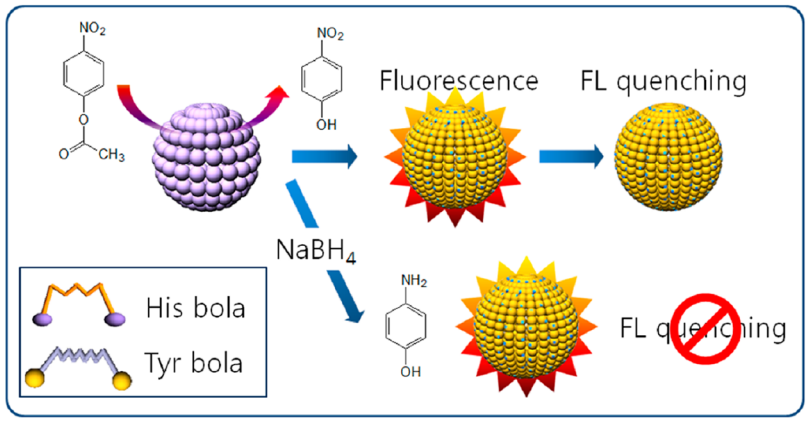
Received: April 24, 2015
Accepted: June 8, 2015
Published: June 8, 2015

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150−14156

Scheme 1. Schematic Layout of the Catalytic and Sensing Cascades: (a) Structures of His and Tyr Bolaamphiphiles and Illustrations of Their Biochemical Moieties on the Surface of Self-Assemblies[a] and (b) Cartoon of the Cascade Catalytic Hydrolysis-Monitoring System Responding to the *p*-NPA[b]



(a)



(b)

[a]The His and Tyr moieties work as a catalytic active site (left) and a sensing probe that selectively binds with *p*-NP (right), respectively. [b]Fluorescence quenching can be interrupted by the conversion of *p*-NP to *p*-AP using $NaBH_4$.

site of a target ion with specific recognition.[15,16] This photoluminescent TyrSA is a promising fluorescent probe for monitoring of the reaction progress because the surface-exposed tyrosine moiety could also function as a selective binding motif of a target organic compound, *p*-nitrophenol (*p*-NP), because of their structural similarity. The phenolic structure facilitates the access of *p*-NP to TyrSA. The nitro group would effectively quench photoluminescence because its acceptance of the excited electron is more favorable than the luminescence emission.[17] The combination of these two bolaamphiphilic self-assemblies offers a facile way to construct a hydrolysis reaction and a subsequent cascade monitoring system from the bolaamphiphilic self-assemblies.

In the present study, we demonstrate the preparation of a reaction and cascade monitoring system made solely of peptidic bolaamphiphilic self-assemblies, which hydrolyze the *p*-nitrophenyl acetate (*p*-NPA) substrate and display the progress of the hydrolysis reaction. A schematic layout of the reaction-monitoring system is shown in Scheme 1b. The catalytic HisSAs hydrolyze the substrate of *p*-NPA to produce *p*-NP, which subsequently quenches the photoluminescence of TyrSA, enabling optical monitoring of the progress of *p*-NPA hydrolysis. The reaction progress was monitored by variation in the concentration of catalytic HisSAs. The sensing of *p*-NP by photoluminescence from TyrSAs was independently adjustable by converting *p*-NP to *p*-aminophenol (*p*-AP), which may not quench photoluminescence of the TyrSAs.

EXPERIMENTAL SECTION

Preparation of Catalytic HisSAs and Photoluminescent TyrSAs. Peptidic bolaamphiphiles were synthesized by the bioconjugation of amino acids with azelaic acid, a compound with a central alkyl chain, via a carbodiimide-based conjugational technique. Detailed synthetic protocols of each peptidic bolaamphiphile are reported in the literature.[13,18] Briefly, the amino acid C-termini of histidine and tyrosine were modified to benzyl ester moieties and were then conjugated with azelaic acid through amide bonds. The crude products of the peptidic bolaamphiphiles were purified by repeating crystallization to produce powdered products.

To prepare catalytic HisSAs, synthesized histidyl bolaamphiphile powder was dissolved in pH-controlled water (pH 7.0 ± 0.3) to attain the desired concentration. After this solution was aged overnight at room temperature to complete the self-assembly, 1 μM zinc chloride ($ZnCl_2$; 99%, Sigma-Aldrich) was added to create catalytic Zn active

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150−14156

sites on the HisSAs.[13] The catalytic active sites were created by the coordination of Zn ions with neighboring histidine imidazoles, and these active sites catalytically converted *p*-nitrophenyl acetate (*p*-NPA; 99%, Fluka) to *p*-NP through hydrolysis. Next, the second type of bolaamphiphile molecules based on tyrosine was applied to prepare the photoluminescent probe by self-assembly in the presence of the photoluminescent compounds salicylic acid (SA) and Tb ion (Tb^{3+}). Tyrosyl bolaamphiphile powder was dissolved in a 5 mM SA and terbium(III) chloride hexahydrate ($TbCl_3 \cdot 6H_2O$; 99.9%, Sigma-Aldrich) solution to attain a concentration of 2 mg/mL.[14] Spherical photoluminescent TyrSAs were produced instantaneously when the tyrosyl bolaamphiphile was dissolved.

Catalytic Hydrolysis and Monitoring of *p*-Nitrophenol (*p*-NP). The substrate of *p*-NPA was dissolved in a mixture of acetonitrile and water (1:9 volumetric ratio) to make *p*-NPA miscible. The prepared HisSA and TyrSA aqueous solutions were mixed with the *p*-NPA solution in a 1:1:1 volumetric ratio. The progress of *p*-NPA hydrolysis was monitored by the changes in the photoluminescence intensity, which was monitored by a spectrophotofluorometer (RF-5301PC, Shimadzu Co.; λ_{ex} = 330 nm) equipped with a monochromated Xe lamp. Photoluminescence decay by conversion of *p*-NPA was visualized with a fluorescence microscope (Eclipse Ti–S, Nikon; λ_{ex} = 330 nm). For confirmation of the independent function of each bolaamphiphilic self-assembly, the catalytic reaction and photoluminescence quenching were also monitored in the absence of HisSAs and TyrSAs, respectively. The reduction of *p*-NP to *p*-aminophenol (*p*-AP) was achieved by the addition of $NaBH_4$, which reduced the nitro group to an amino group, removing the electron-accepting moiety of the nitro group of *p*-NP such that photoluminescence quenching is suppressed.

RESULTS AND DISCUSSION

Performance of Each Bolaamphiphilic Self-Assembly. The tyrosyl and histidyl bolaamphiphiles self-assembled to display spherical particle-like morphologies. The average sizes of TyrSA and HisSA were 45.8 and 47.8 nm, respectively, and the size and shape of the bolaamphiphile self-assemblies did not change by the presence of Zn ion and photoluminescent compounds [see the Supporting Information (SI), Figure S1]. Before testing the combinational function of the two bolaamphiphilic self-assemblies, we examined the independent performance of each bolaamphiphilic self-assembly. Detailed reaction mechanisms and catalytic performances of the HisSAs were previously reported in the literature.[13] Briefly, catalytic HisSAs with Zn ion cofactors promoted the nucleophilic attack of *p*-NPA by a hydroxyl group, leading to conversion of *p*-NPA into *p*-NP. Hydrolysis of *p*-NPA was monitored with UV–vis spectroscopy, which demonstrated that the *p*-NP concentration increased linearly with time (see the SI, Figure S2a). Hydrolysis of *p*-NPA progressed continuously with time in the presence of HisSAs, which verifies the catalytic activity of HisSAs. As a control, the influence of TyrSAs on the catalytic reaction was also investigated. *p*-NPA hydrolysis did not occur with TyrSAs, and little change in the absorbance intensity of *p*-NPA occurred with time (see the SI, Figure S2b). Furthermore, the presence of TyrSAs did not significantly interfere with the catalytic hydrolysis function of HisSAs (Figure 1a). The small difference in the *p*-NP concentration was due to the error introduced during reading of the UV–vis absorbance intensity because of scattering from the TyrSAs. These experiments confirmed that the hydrolysis reaction was conducted only by the catalytic HisSAs and the hydrolysis reaction was not affected by the TyrSAs.

Next, we examined the interference of photoluminescence quenching by HisSAs. Photoluminescence from the TyrSAs was quenched by *p*-NP. The electrophilic nitro group of *p*-NP

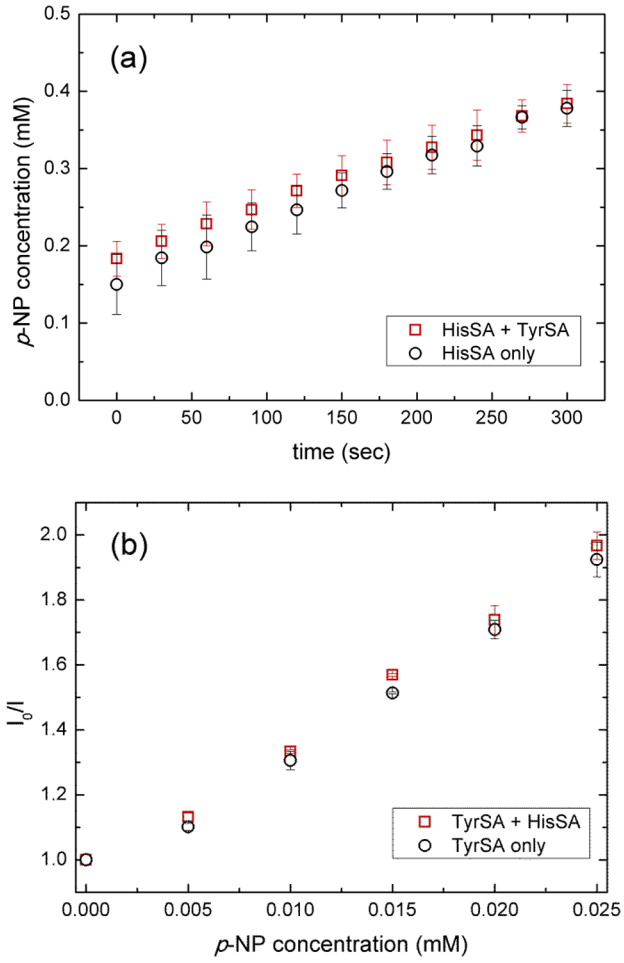


Figure 1. Performances of each bolaamphiphilic self-assembly. (a) Concentration profile of *p*-NP in the presence/absence of TyrSA. The conversion of *p*-NPA was not influenced by the presence of TyrSA. (b) Stern–Volmer plot of the cascade system quenched by *p*-NP. Similarly, the quenching of fluorescence from TyrSA was not influenced by the presence of HisSA.

worked as a photoluminescence quenching moiety, where recombination of the transferred electron occurs without luminescence radiation.[17] Photoluminescence quenching is represented in a Stern–Volmer plot, which is indicative for the degree of luminescence quenching. Photoluminescence from the TyrSAs was sensitively quenched by *p*-NP, showing a linear correlation of the photoluminescence intensity ratios (I_0/I) with increasing *p*-NP concentrations (see the SI, Figure S3a). This linear dependency of photoluminescence quenching on the *p*-NP concentration implies that the TyrSAs are reliable optical indicators for *p*-NP monitoring. The catalytic HisSAs did not show photoluminescence by themselves in that there was no disturbance in the photoluminescence intensity in the *p*-NP and HisSA mixture (see the SI, Figure S3b). In the presence of HisSAs, photoluminescence quenching of the TyrSAs was not affected, showing almost the same degree of quenching degree as that of the native TyrSAs alone (Figure 1b). These experimental results confirmed that these two peptidic bolaamphiphilic self-assemblies worked independently without interfering with one another in the system.

The selectivity of the TyrSAs to *p*-NP against *p*-NPA was examined to confirm that photoluminescence quenching was induced solely by *p*-NP. Photoluminescence from the TyrSAs

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150–14156

was independent of *p*-NPA; it decayed proportionally to the increasing concentration ratio of *p*-NP to *p*-NPA (Figure 2).

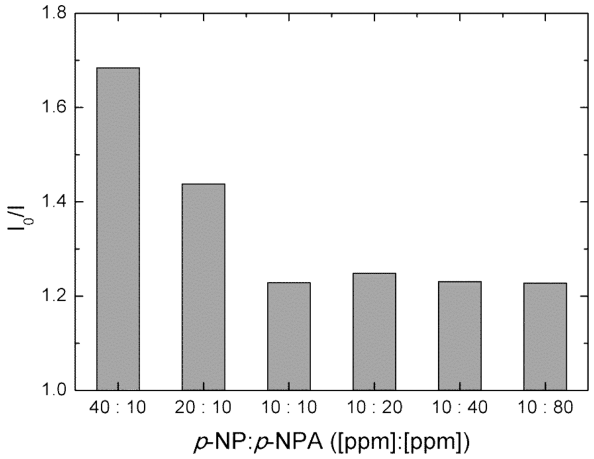


Figure 2. Variations in the quenching degree (I_0/I) with the analyte composition. The invariance of I_0/I with increasing *p*-NPA ratios verifies that fluorescence quenching is dependent only on *p*-NP and not on *p*-NPA.

This selectivity is mainly supposed to originate from the hydrophobic nature of *p*-NPA. Although both *p*-NPA and *p*-NP have nitro groups, access of *p*-NPA to the photoluminescent TyrSAs was retarded by the hydrophobic character of *p*-NPA's acetate group, while the hydrophilic phenolic group of *p*-NP favored association with the TyrSAs. The accessibility arising from the hydrophilicity allowed the transfer of excited electrons from the TyrSAs to *p*-NP, leading to photoluminescence quenching, while the inaccessibility of the TyrSAs to *p*-NPA might prevent photoluminescence quenching.

Monitoring of *p*-NPA Hydrolysis by Photoluminescence Quenching. After verification of the independent performance of each bolaamphiphilic self-assembly without interference, we examined the combinational reaction-monitoring function of the two bolaamphiphilic self-assemblies. As illustrated in Scheme 1b, *p*-NPA was hydrolyzed by the HisSAs, and progression of the hydrolysis was detected by photoluminescence quenching of the TyrSAs. Under the neutral condition of pH 7, the combinational works of HisSAs and TyrSAs functioned well and resulted in linear photoluminescence quenching with time by the generation of *p*-NP. From the degree of quenching, the concentration of *p*-NP that was generated was determined (Figure 3a). This linear increase in the *p*-NP concentration clearly exhibits that the self-assemblies of peptidic bolaamphiphiles enabled the construction of a complex biomimetic system, which included the cascade of a chemical reaction and subsequent visible photoluminescence quenching. The progress of *p*-NPA hydrolysis could also be visualized by photoluminescence quenching, which was observed with fluorescence microscopy (Figure 3b). With the progression of *p*-NPA hydrolysis, photoluminescence decay of the TyrSAs was observed. It is also notable that the spatial proximity of the bolaamphiphilic self-assemblies was not needed to activate the reaction-quenching cascade. The diffusion of the analyte and product in the solution phase was sufficient for the reaction and quenching on the bolaamphiphilic self-assemblies, although some natural enzyme systems have required spatial proximity for the reaction cascade.[19]

Effects of the HisSA and TyrSA Concentrations. Catalytic hydrolysis of *p*-NPA was further investigated with

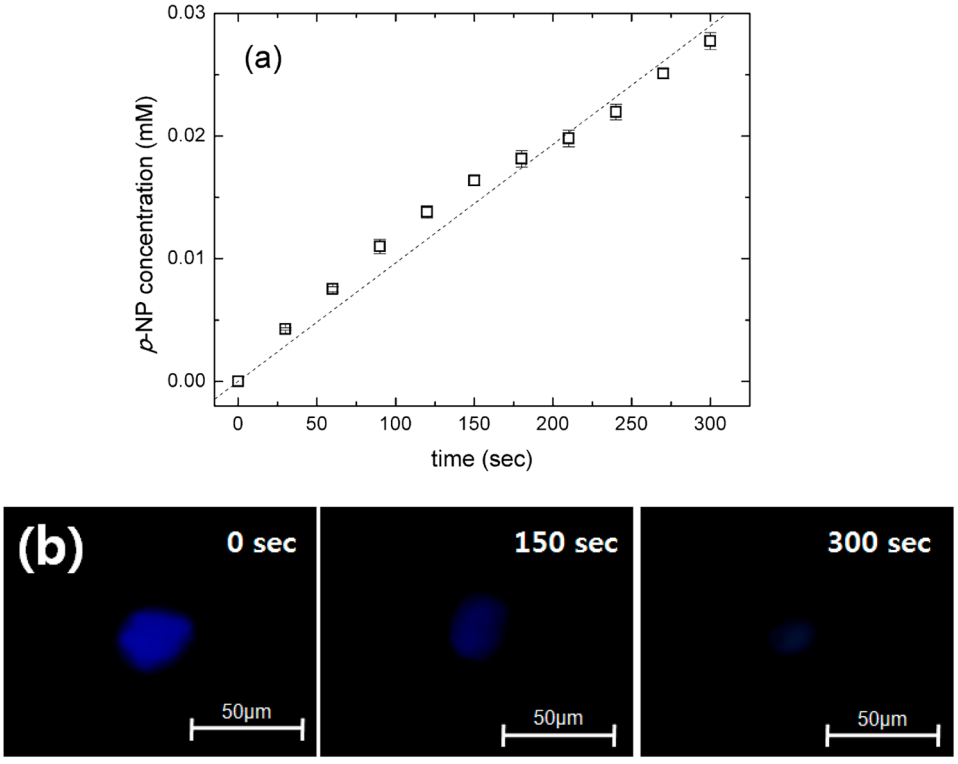


Figure 3. Hydrolysis and sensing of *p*-NPA using the catalysis-sensing cascade system: (a) determination of the *p*-NP concentration with the progression of *p*-NPA hydrolysis; (b) visualization of *p*-NPA hydrolysis by fluorescence quenching.

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150−14156

increasing concentrations of HisSAs, the catalytic self-assemblies. Figure 4a shows the *p*-NP concentration profiles

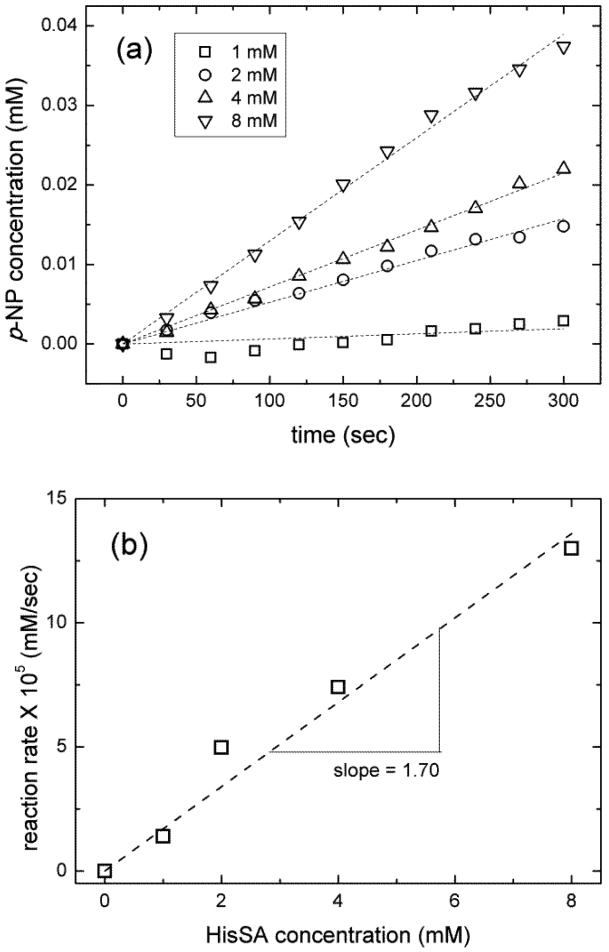


Figure 4. Effect of the HisSA concentration on hydrolysis of *p*-NPA: (a) production of *p*-NP with time under various HisSA concentrations; (b) production rate of *p*-NP with increasing HisSA concentrations.

that were monitored with various concentrations of HisSAs. Obviously, the production of *p*-NP was augmented with increasing HisSA concentrations. As reported previously, the hydrolysis reaction occurs at the active zinc histidine complexes exposed on the surface of the HisSAs.[13] Increased HisSA concentration supplied more catalysts, leading to promotion of the hydrolysis reaction. From the slope of the *p*-NP profile, the hydrolysis reaction rate was determined. As shown in Figure 4b, the reaction rate increased linearly with the concentration of HisSAs. The slope of the reaction rate indicates that the hydrolysis reaction increased at a rate of 1.70×10^{-5} mM/s with respect to the HisSA concentration.

To study the effect of TyrSAs, we examined the sensitivity of photoluminescence quenching with decreasing concentrations of TyrSAs that functioned as photoluminescence probes. As shown in Figure 5a, the sensitivity of the system to *p*-NP increased with decreasing TyrSA concentration. Because the *p*-NP concentration was determined from the photoluminescence intensity ratio (I_0/I), a small quantity of *p*-NP was more sensitively detected at low TyrSA concentrations, where the change in the intensity ratio became significant. The sensitivity of photoluminescence quenching was mainly influenced by the tyrosine phenolic group, which functioned as an association

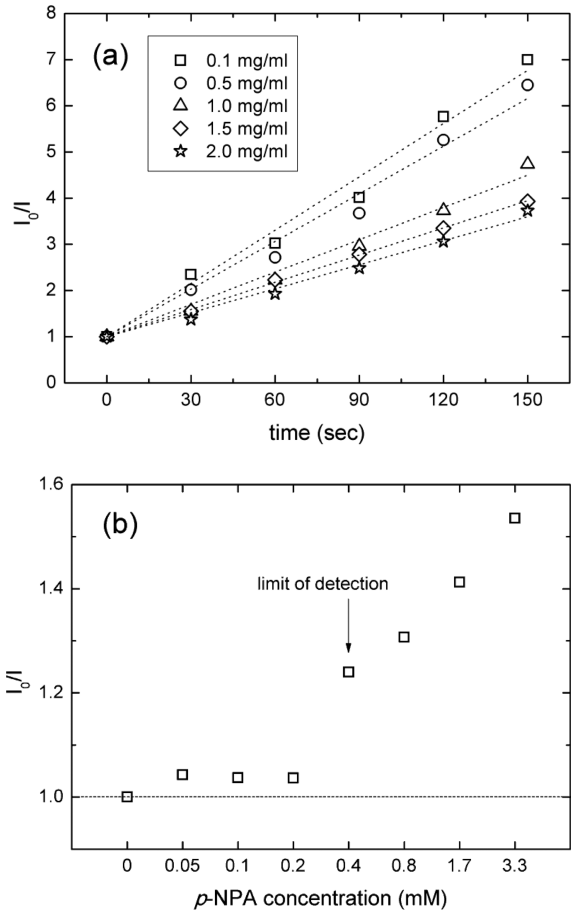


Figure 5. Sensitivity of the catalysis-sensing cascade system: (a) variation in the quenching degree (I_0/I) with decreasing concentration of the TyrSAs; (b) determination of the limit of sensitivity to *p*-NPA. The detection limit is indicated by an arrow at which a considerable increase of I_0/I over 1.10 was observed. The normalized fluorescence intensity (I_0/I) was read 30 s after the addition of *p*-NPA.

moiety of *p*-NP. The association of *p*-NP with TyrSA was mainly driven by the aromatic interaction and was also favored by the presence of the hydroxyl group. The decay of the UV–vis absorbance peak of the Tyr bolaamphiphile after the addition of *p*-NP indicated that these two molecules were associated through the aromatic interaction (see the SI, Figure S4).

The results of the TyrSA-dependent variations in photoluminescence quenching allowed us to determine the limits of sensitivity of the bolaamphiphile system. The sensitivity of the cascade system was determined by monitoring the normalized photoluminescence intensity (I_0/I) at a given time interval of 30 s. We set the tolerance of the normalized intensity as 10% (i.e., I_0/I = 1.10), over which I_0/I was regarded to have relevance. Figure 5b denotes the normalized photoluminescence intensity (I_0/I) that was monitored as the *p*-NPA concentration was varied. The limit of sensitivity for *p*-NPA was determined to be 0.4 mM in a cascade system prepared with HisSAs (2 mM) and TyrSAs (2 mM). At *p*-NPA concentrations under 0.4 mM, I_0/I values were around 1.03, which is indicative of weak sensitivity. I_0/I increased with time even at *p*-NPA concentrations under 0.4 mM, implying further quenching by *p*-NP (data not shown). The limit of sensitivity was not enhanced further even at a lower TyrSA concentration. This is probably due to the sensitivity limit of the

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150–14156

spectrophotofluorometer. When the concentration of TyrSA was lowered, the fluorescence intensity also decayed and accurate reading of the fluorescence intensity became difficult. Thus, a sensible value of I_0/I was obtained over 0.4 mM *p*-NPA (see the SI, Figure S5). However, this result has significance in that this hybrid bolaamphiphile system had considerable sensitivity to the target substrate.

Inhibition of Photoluminescence Quenching by *p*-NP Reduction. Like an inhibitor that impedes the sequential chemical reactions in a biological system, we introduced a reducing agent that converts the nitro group of *p*-NP into an amine group. Because photoluminescence quenching is mainly induced by the electron-accepting nitro group of *p*-NP, conversion of the nitro group into an amino group will prevent quenching of the photoluminescence, as denoted in Scheme 1b. We have examined the inhibition of photoluminescence quenching by $NaBH_4$, which easily converts *p*-NP to *p*-AP. Figure 6 shows changes in photoluminescence quenching with

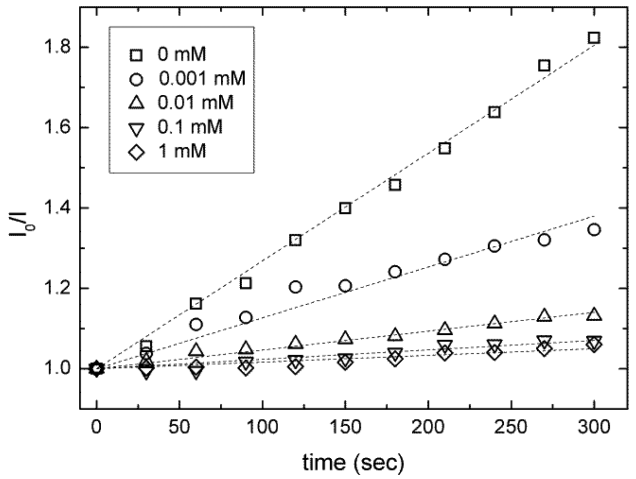


Figure 6. Inhibition of fluorescence quenching by $NaBH_4$. By the addition of $NaBH_4$, *p*-NP was converted to *p*-AP, which does not quench the fluorescence from TyrSA.

increasing concentrations of $NaBH_4$. Photoluminescence quenching was retarded remarkably by the addition of $NaBH_4$, which implies the effective conversion of *p*-NP into *p*-AP. This conversion was augmented with increasing concentrations of $NaBH_4$; however, few differences were observed for concentrations over 0.1 mM, converging the Stern–Volmer plot to 1.0. This is presumably because a $NaBH_4$ concentration over 1 mM is strong enough to fully convert *p*-NP into *p*-AP.

It is also notable that the decrease in photoluminescence quenching was not driven by damage or alteration of the TyrSAs. We investigated the photoluminescence change in the TyrSAs after the addition of $NaBH_4$. The photoluminescence intensity at 545 nm did not change after the addition of $NaBH_4$, suggesting the chemical stability of TyrSA against the reducing agent (see the SI, Figure S6).

CONCLUSION

In conclusion, we demonstrated the combinational use of two bolaamphiphilic self-assemblies for the reaction and monitoring of *p*-NPA hydrolysis. Two designer bolaamphiphilic self-assemblies with biochemical functional groups functioned independently as a catalyst and a photoluminescent probe, respectively, leading to visual detection of the reaction progress with the naked eye. Although there are many enzyme-based reactions that have been developed and their reactions have been monitored using various spectroscopic methods, this approach proved the concept that such a multiple-function system can be constructed using molecular self-assemblies, mimicking a biochemical reaction. The combinational bolaamphiphilic self-assemblies could be applied to a visual sensor device, where an invisible substance is converted and subsequently detected without costly devices. We expect that this cascade system will be applicable for the development of nitroaromatic compounds that can be hydrolyzed. Furthermore, combinational function with other enzymes or catalysts would expand the usage of functional bolaamphiphilic self-assemblies.

ASSOCIATED CONTENT

Supporting Information

SEM images, hydrolysis of *p*-NPA by HisSA, detection of *p*-NP by TyrSA, aromatic stacking between *p*-NP and Tyr bolaamphiphile, limit of sensitivity, and stability of photoluminescent TrySA. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03557.

AUTHOR INFORMATION

Corresponding Author

*E-mail: leessy@yonsei.ac.kr. Tel: +82-2-2123-5758. Fax: +82-2-312-6401.

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a grant from the Korean Research Foundation, which is funded by the Korean government (Grant NRF-2013R1A1A2006459).

REFERENCES

(1) Fuhrhop, J.-H.; Wang, T. Bolaamphiphiles. *Chem. Rev.* **2004**, *104*, 2901–2937.

(2) Shimizu, T.; Masuda, M.; Minamikawa, H. Supramolecular Nanotube Architectures Based on Amphiphilic Molecules. *Chem. Rev.* **2005**, *105*, 1401–1443.

(3) Shimizu, T.; Minamikawa, H.; Kogiso, M.; Aoyagi, M.; Kameta, N.; Ding, W.; Masuda, M. Self-Organized Nanotube Materials and Their Application in Bioengineering. *Polym. J.* **2014**, *46*, 831–858.

(4) Wamberg, M. C.; Wieczorek, R.; Brier, S. B.; de Vries, J. W.; Kwak, M.; Herrmann, A.; Monnard, P.-A. Functionalization of Fatty Acid Vesicles through Newly Synthesized Bolaamphiphilie–DNA Conjugates. *Bioconjugate Chem.* **2014**, *25*, 1678–1688.

(5) Lee, I.; Dong, H.; Lee, S.-Y. Preparation of polypyrrole Microtubules by Selective Deposition on Peptide-Decorated Microtubular Templates. *Curr. Appl. Phys.* **2009**, *9*, E246–E248.

(6) Spear, R. L.; Tamayev, R.; Fath, K. R.; Banerjee, I. A. Templated Growth of Calcium Phosphate on Tyrosine Derived Microtubules and Their Biocompatibility. *Colloids Surf., B* **2007**, *60*, 158–166.

(7) Rufo, C. M.; Moroz, Y. S.; Moroz, O. V.; Stöhr, J.; Smith, T. A.; Hu, X.; DeGardo, W. F.; Korendovych, I. V. Short Peptides Self-Assemble to Produce Catalytic Amyloids. *Nat. Chem.* **2014**, *6*, 303–309.

(8) Jang, H.-S.; Lee, J.-H.; Park, Y.-S.; Kim, Y.-O.; Park, J.; Yang, T.-Y.; Jin, K.; Lee, J.; Park, S.; You, J. M.; Jeong, K.-W.; Shin, A.; Oh, I.-S.; Kwon, M.-K.; Kim, Y.-I.; Cho, H.-H.; Han, H. N.; Kim, Y.; Chang, Y.

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150–14156

H.; Paik, S. R.; Nam, K. T.; Lee, Y.-S. Tyrosine-Mediated Two-Dimensional Peptide Assembly and Its Role as a Bio-Inspired Catalytic Scaffold. *Nat. Commun.* **2014**, *5*, 3665.
(9) Hamley, I. W. Peptide Nanotubes. *Angew. Chem., Int. Ed.* **2014**, *53*, 6866−6881.
(10) Kwak, J.; Lee, S.-Y. Use of Tyrosyl Bolaamphiphile Self-Assembly as a Biochemically Reactive Support for the Creation of Palladium Catalysts. *ACS Appl. Mater. Interfaces* **2014**, *6*, 6461−6468.
(11) Liu, Y.; Wang, T.; Liu, M. Supramolecular Polymer Hydrogels form Bolaamphiphilic L-Histidine and Benzene Dicarboxylic Acids: Thixotropy and Significant Enhancement of Eu^{III} Fluorescence. *Chem.—Eur. J.* **2012**, *18*, 14650−14659.
(12) Liu, Y.; Wang, T.; Li, Z.; Liu, M. Copper(II) Ion Selective and Strong Acid-Tolerable Hydrogels Formed by an L-Histidine ester terminated Bolaamphiphile: from Single Molecular Thick Nanofibers to Single-Wall Nanotubes. *Chem. Commun.* **2013**, *49*, 4767−4769.
(13) Kim, M.-C.; Lee, S.-Y. Carbonic Anhydrase−Mimetic Bolaamphiphile Self-Assembly for CO_2 Hydration and Sequestration. *Chem.—Eur. J.* **2014**, *20*, 17019−17024.
(14) Kwak, J.; Lee, S.-Y. Enhanced Photoluminescence by Tyrosine-Containing Bolaamphiphile Self-Assembly. *Langmuir* **2013**, *29*, 4477−4484.
(15) Kim, S.; Kwak, J.; Lee, S.-Y. Monitoring of Photoluminescence Decay by Alkali and Alkaline Earth Metal Cations Using a Photoluminescent Bolaamphiphile Self-Assembly as an Optical Probe. *Colloids Surf., B* **2014**, *117*, 252−257.
(16) Kim, S.; Kwak, J.; Lee, S.-Y. Optical Sensing of Copper(II) Ions Using a Biofunctional Bolaamphiphile Self-Assembly: Selective Binding of Copper(II) Ions to Tyrosine Moieties. *Sens. Actuators, B* **2014**, *203*, 483−489.
(17) Germain, M. E.; Knapp, M. J. Discrimination of Nitroaromatics and Explosives Mimics by a Fluorescent Zn(salicylaldimine) Sensor Array. *J. Am. Chem. Soc.* **2008**, *130*, 5422−5423.
(18) Kwak, J.; Park, S.-I.; Lee, S.-Y. Use of the Self-Assembly of Tyrosine-Containing Bolaamphiphile Molecules as a Reactive Template for Metal Deposition. *Colloids Surf., B* **2013**, *102*, 70−75.
(19) Wilner, O. I.; Shimron, S.; Weizmann, Y.; Wang, Z.-G.; Willner, I. Self-Assembly of Enzymes on DNA Scaffolds: En Route to Biocatalytic Cascades and the Synthesis of Metallic Nanowires. *Nano Lett.* **2009**, *9*, 2040−2043.

DOI: 10.1021/acsami.5b03557
ACS Appl. Mater. Interfaces 2015, 7, 14150−14156