Photoswitching, Umpolung and Reversible Self-Assembly of Gold Nanoparticles Covered With Thiolated Donor-Acceptor Stenhouse Adducts

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Keywords: photoswitches • immobilization • nanoparticles • self-assembly • polarity reversal

Abstract: The possibility of incorporating functional groups into molecular photoswitches is a prerequisite for their versatility and broad-range applications. Herein we present the first successful synthesis of DASA chromophores featuring a thiol group. The latter provides a unique opportunity to investigate the photoswitching behavior of these visible-light operating chromophores on the surface of metallic nanoparticles. This behavior can be modulated by irradiation time, solvent composition, DASAs population, and the organic layer underneath the chromophores. Moreover, the changes in polarity induced by DASAs photoisomerization are translated onto the colloidal particles giving rise to unusual interfacial and bulk-phase phenomena, including nonlinear solubility effects and reversible agglomeration that takes place in a time-controllable fashion. These findings pave the way for the rational design of new photoresponsive and smart materials.

Introduction

The photoisomerization of organic chromophores is an elegant means to reversibly manipulate the property of matter with spatiotemporal precision and without the generation of chemical wastes.\cite{1} Light-triggered reaction cascades occurring within living cells regulate ion transport in bacteria\cite{2} and provide animal vision.\cite{3} Similar mechanisms are implemented by humans for creating smart functional materials\cite{4} and catalytic systems.\cite{5} To this end, artificial photoswitches responding to specific wavelengths of electromagnetic radiation are being continually designed.\cite{6} The most demanded photoswitches are nowadays those operating in the visible light region due to little harm it exerts to organic and biomolecules.\cite{7} Donor-acceptor Stenhouse adducts (DASAs) are arguably one of the most promising photoswitches synthesized recently.\cite{8} The advantage of DASA, apart from the negative photochromism, is that the isomerization is accompanied by large conformation and polarity changes, where a nonpolar linear isomer is transformed into a polar cyclic form with visible (green) light and reverted upon thermal equilibration in the dark. A serious drawback of this photoswitch is the lack of a thiol function and therefore the inability to form self-assembling monolayers (SAMs), which is the main tool for interfacing inorganic and (bio)organic matter across different length scales – from the nanoscale to the macroscopic level.\cite{9} Moreover, all to date attempts to merge this function with the chromophore have ended in a fiasco.

Difficulties with obtaining a thiol-functionalized DASA were first reported by Klajn and co-workers.\cite{10} The introduction of a thiol group has also long been unsuccessfully endeavored in our group. Each time furan derivatives, the precursors of DASA, were mixed with aminothiols, severe decomposition was observed. This was quite surprising as the thiol group is too weak nucleophile to compete with amine for the opening of furan ring leading to DASA.\cite{11} Some light on the problem was shed recently by the Barner-Kowollik group, who revealed that DASA undergoes thiol-Michael addition, especially when being in the closed form.\cite{12} We therefore surmised that shifting the equilibrium toward the linear isomer would alleviate side reactions and enable the synthesis of thiolated DASA.
Results and Discussion

The population of the linear isomer is highest in the dark; however, it can be completely changed by a solvent.\(^{[13]}\) The original procedure involved THF as a reaction medium as it provided fast reaction times and high yields.\(^{[14]}\) This solvent, however, failed during our initial efforts on synthesizing thiolated DASA. The same authors noted that polar solvents, to which THF could be attributed, stabilize the closed form, which might be the reason for the failure with the thiol group. Accordingly, we have focused on less polar solvents. The optimization was performed on a furfural coupled 1,3-dimethylbarbituric acid and an 11-carbon aliphatic thiol terminated with methyamine (Figure 1A-B). The latter was used in the form of hydrochloride salt because of the instability of unprotected aminothiol, which oxidized instantaneously to disulfide. The free amine was generated in situ by deprotonation with base. Interestingly, the protective gas atmosphere in such an approach was nearly unnecessary; traces of disulfide appeared only after a prolonged time. Among different bases (Na\(_2\)CO\(_3\), Et\(_3\)N) tested, the best result was achieved with DBU (1.5 eq.). It ensured the reaction homogeneity and was sufficiently basic (pKa ~ 13.5) to deprotonate the secondary amine group (pKa ~ 10.8). The desired product (termed 11-thio-N-DASA) was observed in all solvents mediums except for THF (mainly colorless products were formed). Unexpectedly, the reaction proceeded well in polar acetone, suggesting that solvent polarity is not the only reason affecting the formation of DASA. In toluene, which favors both isomers, reaction observation was obscured by precipitation. The most efficient reaction was in DCM and chloroform, which stabilize the opened form. The reaction proceeded quickly (ca. 15 min) and fairly clean (one major product) but not quantitatively. Attempts to increase the product yield by heating the chlorinated solvent mixtures (up to 70°C) or extending the reaction time (several hours) were futile resulting in the formation of by-products. Adding more equivalents of DBU caused reaction decoloration and the disappearance of the product on the TLC plate. The highest yield obtained after column chromatography was 22%. The optimized reaction conditions were then employed for homologous aminothiols (Figure 1C); notably, regardless of the substrate and DASA precursor used (vide infra), the yields appeared comparable (see SI).

![Figure 1. A) The general route toward thiolated DASAs and TLC plate showing the progress of the reaction ~ 15 min after the outset in different solvent mixtures; B) Interconversion between the ring-opened and closed forms of 11-thio-N-DASA on which the reaction optimization was carried out (on the left is the isomerization process, on the right ~ UV-Vis spectra recorded under alternating light and dark conditions and the number of cycles performed). Not full conversion upon irradiation seen in the absorption spectra is explained by the fast back isomerization (it took ~ 33 s to record a full range spectrum); C) List of additional DASA ligands synthesized (by changing the length of aliphatic spacer and the type of heterocyclic core) using the developed protocol and co-ligands employed for the creation of self-assembling monolayers on the surface of gold nanoparticles.]

Interestingly, once isolated, the product is stable. The half-life of 11-thio-N-DASA in toluene, as judged from absorption spectra, is close to 24 h (Figure S1, SI). Conversely, in THF, the product is exceptionally vulnerable, losing half of the initial absorbance within just 10 min (Figure S2, SI). This is consistent with what we observed during the reaction optimization. Importantly, the isolated DASA is reversibly isomerized in toluene (Figure 1B) with only ~1.6% loss of intensity per cycle (1 min irradiation with 570 nm 3 W LED at a distance of 1 cm followed by relaxation in the dark at rt for 5 min); for comparison, thiolated spiropyran (thio-SP), a benchmark photoswitch featuring similar isomerization behavior, decomposes already after the first (UV light) illumination.\(^{[15]}\)

The utility and functionality of 11-thio-N-DASA were probed on gold nanoparticles (AuNPs). We have long interested in the development of light-regulated colloids,\(^{[16]}\) but highly desirable green light-responsive nanoparticles, needed to construct orthogonal and biocompatible systems, were lacking. NP activation has been so far possible only in a very narrow spectral window comprising ultraviolet and blue light (i.a. by using thio-SP).\(^{[17]}\) Trials to install DASA on the surface of magnetite (Fe\(_3\)O\(_4\)) NPs resulted in irreversible bleaching of the chromophore.\(^{[10]}\) A similar effect was also observed on polymer surfaces.\(^{[18]}\) In both cases, bleaching was accounted for the lateral stabilization of the zwitieronic forms of immobilized DASAs. We thus reckoned that distancing DASA molecules on the nanoparticle surface should mitigate the adverse interactions and enable their reversible isomerization.
Figure 2. Absorption spectra of gold NPs covered with mixed 11-thio-N-DASA and UDT monolayers exposed to green light followed by incubation in the dark (plasmon and chromophore band are centred at ~ 527 nm and ~ 570 nm, respectively). When the amount of DASA is low ($\chi$ = ~ 0.1), the switching of the chromophore can be performed fast and many times in a row (top left). With increasing of the population of DASA, the responsiveness (time, top right, and the degree of isomerization, both for the forward, bottom right, and back process, bottom left) of the NPs decreases due to electrostatic interactions and steric constraints exerted by the chromophore. In all cases, irrespective of the conditions, the NPs remain stable and dispersed in the solution.

We began our study with ~6 nm AuNPs. Functionalization was performed via the exchange of a dodecylamine stabilizing layer on 11-thio-N-DASA (SI). The population of DASA ligand on the nanoparticle surface was regulated with 1-undecanethiol (UDT) as co-ligand. When the content of the immobilized DASA is low ($\chi$ = 0.1, where $\chi = n_{\text{DASA}}/(n_{\text{DASA}}+n_{\text{UDT}})$), the chromophore behaves as one freely diffusing in the solution (Figure 2A). The isomerization occurs reversibly over 6 min per cycle (in total 5 cycles were performed) without any considerable fatigue. At $\chi$ = 0.2, the process is still reversible, but the time needed for DASA to return to the native state triples (9 minutes, instead of the initial 3 minutes, Figure 2B). This indicates that the isomerized DASA termini are beginning to stabilize by electrostatic interactions. Further increase of the DASA population ($\chi$ = 0.3) causes a fraction of DASA ligands to “freeze” in the zwitterionic form after the isomerization (Figure 2C). At contents $\chi$ > 0.5, the crowdedness is so large that only a small portion of DASA is able to respond to light and, once isomerized, practically does not revert back (Figure 2D).

Figure 3. Absorption spectra of gold NPs covered with mixed 11-thio-O-DASA and UDT monolayers (top image, plasmon, and the overlaid chromophore bands are centered at ~ 527 nm and ~ 542 nm) and vector cartoon chart (bottom image) demonstrating colloidal stability of the NPs under irradiation. The stability depends on the population of the immobilized DASA and the efficiency of the photoisomerization reaction. As the population of DASA increases ($\chi$ = ~ 0.1 - 0.3), an increasing amount of highly polar zwitterionic isomer is formed, which leads to the destabilization of the NPs. At some point ($\chi$ = ~ 0.3 – 0.5), this trend is reversing, as there is no more room for all DASA ligands to isomerize; consequently, the stability of the NPs is restored. Further increase of the DASA population ($\chi$ approaches to 1) leads to the inherent instability of the NPs caused by the polar character of the non-isomerized chromophore.
As opposed to the previous reports, the obtained 11-thio-N-DASA coatings are quite robust, especially when diluted with co-ligands. After 24h, the NPs with the coverage of 10% of the chromophore are still able to reversibly isomerize, showing almost the same absorbance profile as at the beginning (Figure S4, SI). Despite the overall reversibility, the NPs do not undergo any appreciable changes in their physical appearance (e.g., dissolution-precipitation), which could be expected from switching between two isomers with different polarities. We hypothesized that the polarity changes induced by 11-thio-N-DASA are insufficient to be effectively translated onto the NPs. Therefore, we modified the heterocyclic core of the chromophore and synthesized a new DASA ligand (11-thio-O-DASA) using Meldrum’s acid. Indeed, the NPs decorated with 11-thio-O-DASA appear more polar than their predecessors, and display a signature of aggregation already at low DASA coverages (χ = 0.1), manifested through the bathochromic shift of the right shoulder of the plasmon band, after the chromophore being reversibly isomerized from the zwitterionic to the neutral form (Figure 3). With increasing the DASA coverage (0.1 < χ < 0.5), the aggregation is aggravating. At some point (χ ~ 0.5), an unexpected reversal in polarity takes place, and the photoswitched NPs are getting stable. We attribute this to the low conversion of one isomer to the other due to the high density of DASA monolayer and ensuing steric constraints. Further increase of the amount of DASA (χ ~ 1) renders the NPs unstable again, which aggregate prior to irradiating the sample. The change in polarity, in this case, is solely due to the abundance of the neat DASA. In all cases, the aggregation is irreversible; changing the solvent, increasing the temperature, shaking the sample do not recover the system. We thus supposed that this is due to excessive intraparticle stabilization of the isomerized DASA termini and that further increasing the distance between them should weaken these interactions.

To this end, we synthesized a 18-thio-O-DASA by elongating the spacer between the thiol and the chromophore to 18 carbons. We also varied the length (8, 11, and 16 carbons) and the bulkiness of the end groups (Me → Ph) of the background ligands. We found that the NPs undergo deaggregation only when the ligands surrounding the chromophore are sufficiently short (8, 11 carbons), not bulky (Me), and the amount of the chromophore is in a range of 0.05 < χ < 0.2 (Figure 4). This is in contrast to what has been observed for thio-SP functionalized NPs, where shorter co-ligands worsened the ability of the particles to disintegrate. We are inclined to think that this may be due to different mechanisms of NP aggregation and deaggregation. We assume that in our case the enlargement of the interligand space allows the solvent molecules to solvate the ligands more efficiently and surmount the attractive (Van der Waals and Coulombic) interactions between them. The better exposure of DASA to the solvent is corroborated by the apparent increase in polarity of the NPs with the same DASA/co-ligand molar ratios, but the larger separation between the chromophore and the underlying organic monolayer. The degree of the NP deaggregation for 1-octanethiol as co-ligand (χ = 0.05) was estimated from a half-width at half maximum (HWHM) of the plasmon band as 52%. In the chloroform-toluene mixture (1:4 v/v), this factor increases to 55% (Figure 5, for more details see SI), indicating better solvation of the NPs. There are, at least, two reasons for the incompleteness of deaggregation. First, the sedimentation of larger agglomerates, which can be accelerated by manual shaking. Second, massive adhering of the NPs to the walls of a measurement vial owing to attractive interactions between zwitterionic DASA ligands and the polar quartz surface. The deaggregation of the NPs obeys first-order kinetics with the rate of 9.4x10⁻⁴ s⁻¹ (the chloroform additive increases the rate to 1.4x10⁻³ s⁻¹), and it takes more than 40 min for the NPs to reach the equilibrium. We wondered if this time could be reduced, and resorted thus back to thio-N-DASA that exhibits faster isomerization kinetics.
Figure 5. Light-induced self-assembly of gold NPs covered with a mixture of 18-thio-O-DASA (χ = 0.05) and OT: (A) cartoon representation, (B) absorbance spectra showing reversibility (upper row) and dependence of aggregation on irradiation time (middle row) and the composition of the solvent mixture (left vs. right column). Kinetic traces of aggregation-deaggregation are shown in the bottom row. The more polar the solvent, the lesser the aggregation, and the larger degree of deaggregation. This can be rationalized by better solvation properties of chloroform used as an admixture in toluene. Note that at high chloroform contents (> 40% v/v), the photoisomerization, and consequently, the aggregation practically does not occur.

Figure 6. Light-induced reversible self-assembly of gold NPs covered with a mixture of 18-thio-N-DASA (χ = 0.1) and OT: cartoon representation (A), absorbance spectra and kinetic traces (B), TEM micrographs (C). Bottom-right photograph depicts blurring of initially sharp edges of a NP aggregate due to the detachment of the NPs under thermal relaxation in the dark. For comparison, aggregation of the NPs covered with 18-thio-O-DASA (χ = 0.05) and OT are shown in D (TEM images) and E (photographs of the NPs in solution). Bottom-left pictures (small scattered NP clusters vs. hexagonally ordered NP rafts) indicate different propensity of the NPs towards the aggregation in the solution.

We prepared NPs decorated with an 18 carbon ligand (18-thio-N-DASA) in a ratio of 1:9 with 1-octanthiol. Indeed, the obtained NPs are characterized not only by a faster time of disassembly (~ 20 min, k = 2.6 x 10^3 s^-1) but also do this to a higher degree (~ 78%, Figure 6). As the surface coverages for both types of NPs are similar, we speculate that the differences stem from the nature of the heterocyclic ring and its ability to stabilize the zwitterionic form of the chromophore. Indeed, microscopy images revealed that the NPs with the non-isomerized 18-thio-N-DASAs tend to disperse better over a TEM grid than those covered with 18-thio-O-DASA. Upon irradiation, both types of NPs gather into spheroidal, interconnected clumps achieving several hundred nm in size. The relative content of free and agglomerated NPs seen on TEM pictures corresponds roughly to the extent of aggregation seen on UV-Vis spectra. Once the light source is removed, the NPs return to the dispersed state. The diffusion of the NPs from the parent aggregates can be observed as the transition from multilayer structure to monolayer structure and eventually spasing of the latter. The process of the assembly-disassembly can also be easily followed by the naked eye through the red-to-pink-grey color change of the NP dispersions.
Conclusion

In summary, we developed the first synthetic protocol to couple the thiol group with DASA chromophores. This allowed us to study the behavior of DASAs on the surface of metallic (Au) nanoparticles. The immobilized DASAs, unlike the free ones, are easy to control upon photoisomerization. The degree and rate of the latter can be precisely tuned by irradiation time, solvent composition, DASAs population, and the organic layer underneath the chromophores. What is more, the polarity changes occurring at DASAs can be translated onto the nanoparticles. Remarkably, these changes are not always commensurate with the amount of the adsorbed chromophores. The polarity of the nanoparticles can change nonlinearly – from prime instability followed by the island of stability, i.e., kind of “nanoscale umpolung”, to ultimate instability. Moreover, it is also possible to control the timescale and degree at which nanoparticles aggregate. The self-assembly process can be fast and slow depending on the nature of the heterocyclic skeleton of DASAs and the solvent polarity changes occurring at DASAs. What is more, the assembly process can be fast and slow depending on the nature of the heterocyclic skeleton of DASAs and the solvent polarity changes occurring at DASAs.

Supporting information for this article is available from the Online Library or from the author.

Acknowledgements

This work was funded by the National Science Centre of Poland (grant SONATA BIS 4 no. 2014/14/E/ST5/00778). TEM pictures were taken in the Center of Synthesis and Analysis BioNanoTechno of University of Bialystok, the equipment was funded by the EU as part of the Operational Program Development of Eastern Poland 2007–2013, project: POPW.01.03.00–20–034/09–00.

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