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Logic Gates

Resettable, Multi-Readout Logic Gates Based on Controllably Reversible Aggregation of Gold Nanoparticles**

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In recent years, more and more chemical systems have been employed to perform Boolean logic operations, resulting in the remarkable progress of various molecule-based logic systems, such as AND, OR, XOR, NAND, NOR, INHIBIT, half-adder, and half-subtractor.[1] The set–reset function in molecular digital systems is an important step to construct memory elements of sequential logic operations that have the possibility to store information in a write–read–erasable form.[2] Most of reported molecular logic gates have the following disadvantages: 1) they are not resettable; and 2) they employ small molecules or biomacromolecules as inputs and a fluorescent signal as the output, which relies on advanced instruments for the readout.[3] Gold nanoparticles (AuNPs) have recently attracted considerable attention because of their many distinctive physical and optical properties. In particular, the surface plasmon resonance (SPR) of AuNPs can be changed by modulating the distance between AuNPs, along with the color change of AuNPs solutions.[4] Therefore, by using AuNPs, the molecular events in logic systems can be easily transformed into color changes, which can be monitored by the naked eye. Moreover, the change of dispersion states of AuNPs can be further monitored by other tools such as UV/Vis spectra, zeta potential, and dynamic light scattering (DLS), which in turn can be applied as output signals. Herein we present a resettable and multi-readout logic system capable of several types of logic operations based on the aggregation of spiropyran-modified gold nanoparticles (spiropyran-AuNPs) in aqueous media.

Spiropyrans are an important class of photoswitchable organic molecules. Under dark conditions or exposure to visible light, the spiropyrans exist in their colorless, non-planar, and closed form (SP), which can be isomerized to the red, planar, and open merocyanine form (MC) with UV light irradiation by the heterocyclic ring cleavage of the spiro C–O bond.[5] The MC isomer has a phenolate group, which can readily bind with metal ions. The chelated metal ions can be released by visible light irradiation.[6] We expect the closed form of spiropyran-AuNPs to be monodispersed in solutions that exhibit red color; after UV light irradiation followed with the addition of 10 μM of Cu^{2+}, the formation of a sandwich between Cu^{2+} and MC on different AuNPs can cause open merocyanine-modified AuNPs (MC-AuNPs) to aggregate, with a color change from red to purple. We expect that the combination of UV light irradiation and the subsequent addition of Cu^{2+} to spiropyran-AuNPs solutions could be applied to construct an AND logic gate. Moreover, we can apply this system to construct other kinds of logic gates based on various input signals such as different kinds of metal ions and chelating ligands. The aggregates of MC-AuNPs can be redispersed upon exposure to visible light irradiation owing to the open-to-closed isomerization of spiropyran and the release of the "bridge" (metal ions), which generates a resettable AuNP-based logic system (Scheme 1).

To realize the spiropyran-AuNP-based logic gates, we synthesized spiropyran-terminated alkanethiols (Supporting Information, Scheme S1), and tested the isomerization of spiropyran thiols in solution. We prepared the solution of the spiropyran thiols in ethanol at a concentration of 1×10^{-4} M. Spiropyran thiols were stored in the dark overnight at 0 °C, and the majority of the spiropyran molecules existed as the closed colorless isomer, which was switched into the open MC form with UV light irradiation; the maximum absorption at 550 nm was obtained after persistent irradiation for 20 seconds (Supporting Information, Figure S1). Addition of Cu^{2+} (1×10^{-3} M) into the MC solution resulted in a change in the absorbance spectrum, with a new peak appearing at 420 nm along with the decrease of the absorption at 550 nm, which is due to the formation of the MC–ion complex (Supporting Information, Figure S2).[7]

AuNPs were prepared and modified with an alkanethiol terminated in triethylene glycol (EG3) and another alkanethiol terminated in spiropyran (EG3SP; Scheme 1). EG3 thiols were used to mix with EG3SP thiols to increase the water solubility of spiropyran-AuNPs and decrease the density of EG3SP on AuNP surface.[8] The mixed alkanethiols adsorbed onto gold surfaces by means of ligand exchange.[9] We found that if the ratio of EG3SP to EG3 was higher than 1:10, the AuNPs can readily aggregate in the process of preparing spiropyran-AuNPs. Upon decreasing the ratios from 1:10 to 1:100, the spiropyran-AuNPs can be well-

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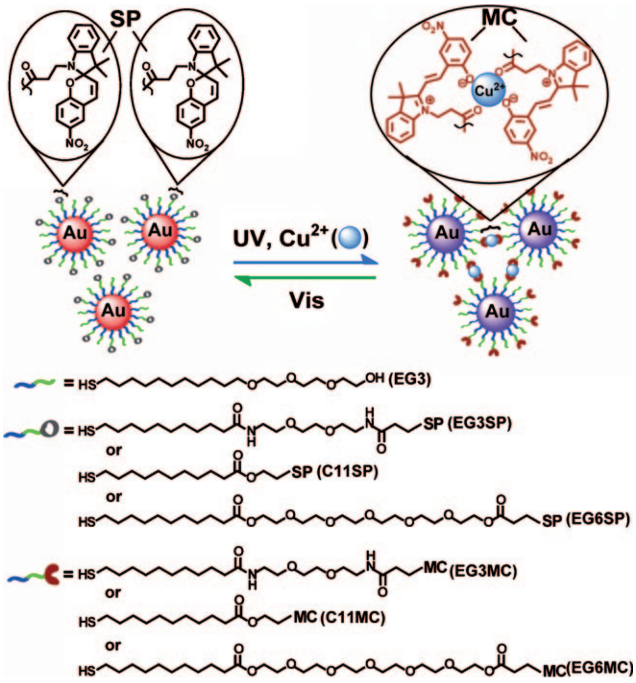
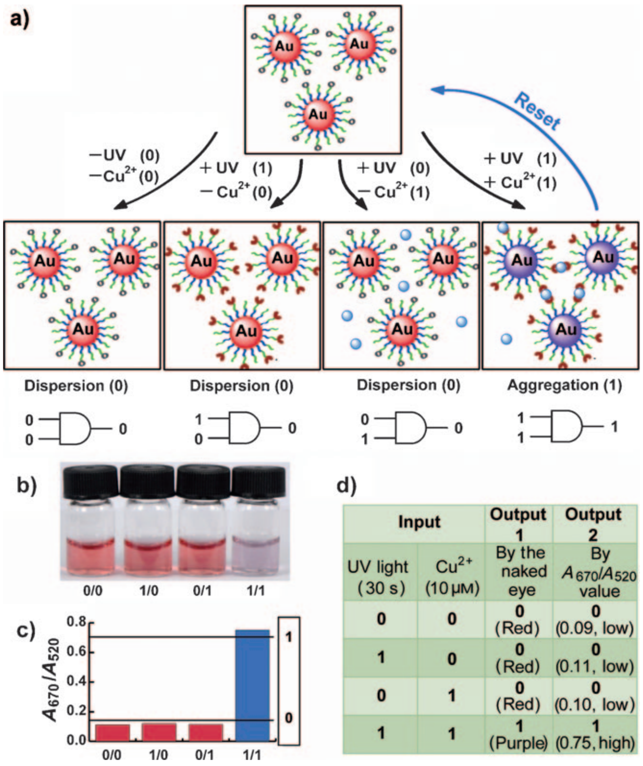


Scheme 1. Proposed mechanism for the photoresponsive control of spiropyran-AuNPs and the molecular structures of stabilizing agents (EG3) and the closed form of spiropyran ligands (C11SP, EG3SP, EG6SP) and their corresponding MC isomers (C11MC, EG3MC, EG6MC). UV light wavelength: 365 nm, visible light: 520 nm. The concentration of Cu^{2+} was 10 μM, and the reversible modulations took place in an aqueous solution (pH 7.0).



Input		Output 1	Output 2
UV light (30 s)	Cu^{2+} (10 μM)	By the naked eye	By A_{670}/A_{520} value
0	0	0 (Red)	0 (0.09, low)
1	0	0 (Red)	0 (0.11, low)
0	1	0 (Red)	0 (0.10, low)
1	1	1 (Purple)	1 (0.75, high)

Figure 1. The spiropyran-AuNP-based resettable AND logic gate. a) Design strategy. In the absence of both inputs (0/0) or in the presence of either input (1/0, 0/1), the spiropyran-AuNPs solutions remained red (output = 0); in the presence of both inputs (1/1), the color of the spiropyran-AuNP solutions changed from red to purple. b) Photograph of AuNP solutions and c) their corresponding UV/Vis absorption. d) A truth table of the AND logic gate.

dispersed in aqueous solution. However, the absorption response relied on the ratios, with relatively high ratios (such as those over 1:20), and the spiropyran-AuNPs aggregated quickly and completely after UV light irradiation followed by the addition of Cu^{2+} ions. If we decreased the ratios (such as to 1:60, 1:100), the spiropyran-AuNPs aggregated incompletely; smaller A_{670}/A_{520} values indicate incomplete aggregation (Supporting Information, Figure S3, where A_{670} is the shoulder absorption band at 670 nm and A_{520} is that at 520 nm). Therefore, we chose 1:10 as the best ratio for subsequent experiments.

Based on the above results, we first designed an AND logic gate that employs 30 s of UV light irradiation and the addition of Cu^{2+} ions (10 μM) as inputs, and the color change of solutions containing spiropyran-AuNPs as the output. With respect to inputs, the presence and absence of UV light irradiation and the addition of Cu^{2+} is defined as "1" and "0", respectively. For output, we define the red solutions containing well-dispersed spiropyran-AuNPs as "0", and the purple solutions containing aggregates of spiropyran-AuNPs as "1". Only the presence of both inputs (1/1) could cause spiropyran-AuNPs to aggregate along with a color change from red to purple (output = 1); while those in the absence of both inputs (0/0) or in the presence of either input (1/0, 0/1) remain red (output = 0; Figure 1 b). Furthermore, the AND logic gate was further confirmed by testing the UV/Vis absorption responses, a higher A_{670}/A_{520} value for the presence of both inputs (1/1) indicated complete aggregation of spiropyran-AuNPs, while the other three much lower A_{670}/A_{520} values for the other kinds of inputs (0/0, 1/0, 0/1, respectively) indicated the dispersion of spiropyran-AuNPs (Figure 1 c,d).

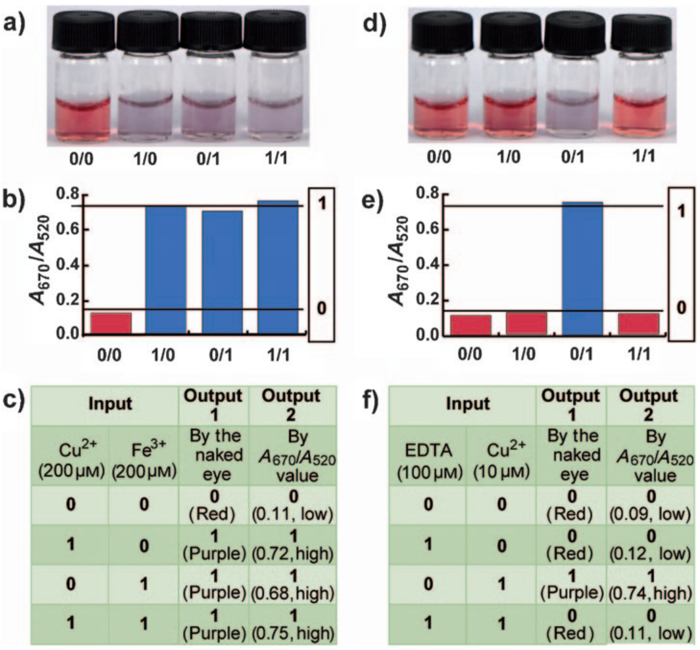
As one of the inputs for this AND logic gate, the choice of metal ions was critical. We investigated the responses of spiropyran-AuNPs in the presence of various metal ions, including Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} (Supporting Information, Figure S4) at concentrations of 10 μM, 30 μM, 60 μM, 100 μM, and 300 μM. When the concentrations of metal ions were higher than 100 μM, almost all kinds of ions can cause the aggregation of the MC-AuNPs. When the concentrations of metal ions were less than 100 μM, only Cu^{2+} caused the aggregation. This result indicates that the selectivity of MC-AuNPs towards Cu^{2+} was concentration-dependent.

To explore the origin of this selectivity toward Cu^{2+}, we performed theoretical calculations using density functional theory (DFT) to evaluate the change of the Gibbs free energy (ΔG) of the interactions between the MC isomers and various metal ions. The result showed that ΔG of Cu^{2+}, Co^{2+}, and Ni^{2+} were much lower than those of other metal ions (Supporting Information, Table S1). The interactions between the MC isomers and Cu^{2+}, Co^{2+}, and Ni^{2+} tend to take place more spontaneously than other metal ions. Furthermore, the water-exchange rate constant of Cu^{2+} is $4.4\times10^{9}\,s^{-1}$, which is much higher than those of Co^{2+} ($3.2\times10^{6}\,s^{-1}$) and Ni^{2+} ($3.2\times$

$10^4\,s^{-1}$),[10] indicating that kinetically, Cu^{2+} has more chance to bind with MC isomers than other metal ions. The analysis based on both thermodynamics and kinetics agrees with our observation that Cu^{2+} has stronger ability than other metal ions to bind with the MC isomer (Supporting Information, Figure S5).

We evaluated the lowest concentration of Cu^{2+} that ensured the functions of the AND logic gate. We added various concentrations of Cu^{2+} (0 μM, 0.1 μM, 0.3 μM, 0.6 μM, 1.0 μM) into MC-AuNP solutions, and found that for the color change from red to purple by an increase of Cu^{2+}, the lowest concentration of Cu^{2+} that can be visualized by the naked eye was 0.3 μM (Supporting Information, Figure S6 A), which was demonstrated by testing their absorption responses (Supporting Information, Figure S6B). Furthermore, we found that different counterions had negligible influences to the chelation between Cu^{2+} and MC on AuNPs (Supporting Information, Figure S7). Owing to the good selectivity and sensitivity, this system has the capacity to detect Cu^{2+} in aqueous media. We note that the US Environmental Protection Agency has set the maximum contaminant level of Cu^{2+} in drinking water to be 20 μM,[11] a value that readily allows naked-eye-based readout by this logic system.

Based on the fact that higher concentrations (>100 μM) of other metal ions such as Fe^{3+} can also induce MC-AuNPs to aggregate, we constructed an OR logic gate by using MC-AuNPs, 200 μM of Fe^{3+}, and 200 μM of Cu^{2+}. We employed the addition of either Fe^{3+} or Cu^{2+} as input and defined the presence and absence of Fe^{3+} or Cu^{2+} as "1" and "0", respectively. The color change of MC-AuNP solution was defined as output. In the presence of either or both inputs (1/0, 0/1, 1/1), the color of MC-AuNPs solution changed from red to purple immediately (output = 1) (Figure 2a), which was further demonstrated by testing their UV/Vis absorption responses, that is, much higher A_{670}/A_{520} values for the inputs (1/0, 0/1, 1/1) than that in the absence of inputs (0/0; Figure 2b,c).



c)

Input		Output 1	Output 2
Cu^{2+} (200 μM)	Fe^{3+} (200 μM)	By the naked eye	By A_{670}/A_{520} value
0	0	0 (Red)	0 (0.11, low)
1	0	1 (Purple)	1 (0.72, high)
0	1	1 (Purple)	1 (0.68, high)
1	1	1 (Purple)	1 (0.75, high)

f)

Input		Output 1	Output 2
EDTA (100 μM)	Cu^{2+} (10 μM)	By the naked eye	By A_{670}/A_{520} value
0	0	0 (Red)	0 (0.09, low)
1	0	0 (Red)	0 (0.12, low)
0	1	1 (Purple)	1 (0.74, high)
1	1	0 (Red)	0 (0.11, low)

Figure 2. The MC-AuNP-based resettable OR (a, b, c) and INHIBIT (d, e, f) logic gates. a) Photograph of MC-AuNP solutions for the OR logic gate in the absence of inputs (0/0) and in the presence of either or both inputs (1/0, 0/1, 1/1), and b) their corresponding UV/Vis absorption responses. c) A truth table of the OR logic gate. d) Photograph of MC-AuNP solutions for the INHIBIT logic gate and e) their corresponding UV/Vis absorption responses. With respect to the inputs (0/0, 1/0, 1/1), the MC-AuNPs solutions remained red (output = 0); only the presence of Cu^{2+} (input = 0/1) led to the color of the MC-AuNP solutions changing from red to purple. f) A truth table of the INHIBIT logic gate.

Based on MC-AuNPs, an INHIBIT logic gate can be created by employing ethylenediaminetetraacetic acid (EDTA, 100 μM) as one input, the addition of 10 μM of Cu^{2+} as another input, and the color change of MC-AuNPs solution was defined as output. The addition of EDTA (input = 1/0) into solutions containing MC-AuNPs cannot lead to aggregation of MC-AuNPs. However, EDTA has much stronger capacity than MC isomers to sequester Cu^{2+}, thus preventing the formation of aggregates in solution containing both MC-AuNPs and Cu^{2+} (input = 1/1). Only the addition of Cu^{2+} (input = 0/1) can cause MC-AuNPs to aggregate (output = 1; Figure 2d). The INHIBIT logic gate was demonstrated by testing the UV/Vis absorption responses, a higher A_{670}/A_{520} value for the presence of Cu^{2+} (input = 0/1) than those for inputs (0/0, 1/0, 1,1) (Figure 2e,f).

Owing to the reversible chemical nature of the spiropyran group, these AuNP-based logic gates could be reset to their initial conditions by visible light, under which the aggregation of spiropyran-AuNPs can be modulated reversibly. We irradiated the aqueous solution containing spiropyran-AuNPs with UV light (30 s); the color of the solution remained red, indicating that MC-AuNPs still remained well-dispersed. After incubating with Cu^{2+} or Fe^{3+} (>100 μM), the color of the solution changed from red to purple immediately. To investigate the reversible potential, aqueous solutions containing aggregates of MC-AuNPs were centrifugated to remove extra Cu^{2+} or Fe^{3+}, to which deionized water was added to disperse the aggregates. To eliminate the H^+-induced aggregation by its interaction with the ether units of EG3 on AuNPs,[12] we adjusted the pH value of the new solution to be slightly basic (pH 9.0–10.0), and irradiated it with visible light (30 s). We found that this treatment led to a change in the color of the solution from purple to red within several minutes; this result is expected because the aggregates were redispersed to be separate spiropyran-AuNPs after the open-to-closed isomerization of spiropyran molecules on gold surfaces.

To further confirm these reversible modulations of spiropyran-AuNP aggregates, we compared the TEM images of spiropyran-AuNPs before and after UV light irradiation followed by the addition of Cu^{2+} (Supporting Information, Figure S8). The spiropyran-AuNPs can be photoswitched between dispersed and aggregated forms by applying UV light irradiation followed with the addition of Cu^{2+} and visible light alternatively at least three times. It is at present difficult to obtain more cycles because of photofatigue of spiropyran on AuNP surfaces.[6c] UV/Vis absorption

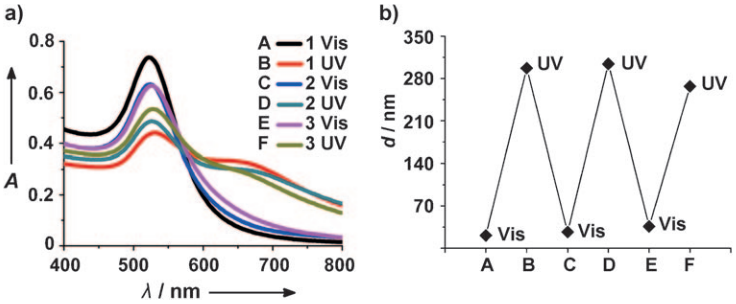


Figure 3. a) UV/Vis absorption spectra reflecting the cycles of UV/visible light irradiation (from a to f, 30 s each). b) The sizes (diameter *d*) of dispersed (A, C, E) and aggregated (B, D, F) spiropyran-AuNPs measured by DLS.

spectra confirmed these reversible processes; that is, with the formation of AuNP aggregates, the absorption band at 520 nm decreased along with the appearance of a new shoulder absorption band at about 670 nm (Figure 3 a, curves of B, D, F). With the redispersion of aggregates after visible light irradiation, the absorption band at 520 nm increased along with the decrease of those at 670 nm (Figure 3 a, curves of A, C, E). The reversible modulations were also supported by the DLS data (Figure 3 b). The average hydrodynamic diameter of well-dispersed spiropyran-AuNPs is about 24 nm, while that of their aggregates increased to be approximately 300 nm, congruent with the TEM analyses.

We also used zeta potential measurements to compare the surface charge on monodispersed spiropyran-AuNPs and their aggregates at pH 7.0. The zeta potential of well-dispersed spiropyran-AuNPs was about −30 mV, while that of their aggregates was approximately 0 mV (Supporting Information, Figure S9). We reasoned that the increase of zeta potentials was due to the positively charged ammonium group on MC isomers, where the phenolate anionic groups chelated with Cu^{2+}. These results from zeta potentials are consistent with those from UV/Vis spectroscopy, TEM, and DLS data. Importantly, we believe that most of the means for characterization, such as UV/Vis spectra, zeta potential, and DLS can serve as output signals in the logic gate, by which a multi-readout logic system could be achieved.

Several factors influence this logic system. First, pH values of the solution can greatly influence the stability of spiropyran-AuNPs. We prepared aqueous solutions containing spiropyran-AuNPs with pH values from 2.0 to 12.0. When the pH values of the solutions decreased below 4.0, the A_{670}/A_{520} values was much higher owing to the aggregation of AuNPs. The ether units of EG3 residing on different AuNPs can protonate, resulting in aggregation.[12] The spiropyran-AuNPs were well-dispersed in aqueous solutions with pH values higher than 4.0 (Supporting Information, Figure S10). Next, we investigated the influence of pH values to this aggregation by characterizing the absorbance responses to various pH values. In the range between pH 4.0 and 8.0, the functionalized AuNPs, capped by the mixture of EG3SP and EG3 with a ratio of 1:10, aggregated in tens of seconds after UV light irradiation and incubation with Cu^{2+}. We note that aggregation of spiropyran-AuNPs was incomplete with the increase of pH values from 8.0, because the negative charges (hydroxide ions) in basic solution can compete with phenolate groups on MC to bind with Cu^{2+}. When the pH value reached 11.0, the binding between Cu^{2+} and MC on Au surfaces cannot take place, and AuNPs remained well-dispersed in aqueous solutions. Thus the optimal pH range for this logic system was from 4.0 to 8.0 (Supporting Information, Figure S11).

To investigate the influence of the length of the units of EG that tethered spiropyran and alkanethiol, we synthesized another two spiropyran ligands containing various lengths of the units of EG (Supporting Information, Scheme S2 and S3), one having no EG (C11SP; Scheme 1), and the other containing six EGs (EG6SP; Scheme 1). We used EG3 as the stabilizing agents for all three kinds of spiropyran ligands (the ratio was 1:10 for all the three ligands to EG3). For the MC-AuNPs having no EG (C11MC-AuNPs), almost no aggregation was observed upon the addition of Cu^{2+} ($10~\mu\mathrm{M}$). We reasoned that the stabilizing agents (EG3) on AuNP surfaces were too long to allow chelation between Cu^{2+} and MC on different C11MC-AuNPs surfaces. On the other hand, when we increased the units of EG to six to form EG6MC-AuNPs, the aggregation was incomplete in the present of Cu^{2+} ($10~\mu\mathrm{M}$). We reasoned that the EG6 tether was longer than EG3, thus providing more flexibility for MC groups on EG6MC-AuNP surfaces; some MC groups on different EG6MC-AuNPs bind with Cu^{2+} to enhance the chances of aggregation, while the other MC groups on the same EG6MC-AuNPs can also have room to bind with Cu^{2+} owing to the flexible and long tether, thus resulting in reduced aggregation. Therefore, EG3SP was the best spiropyran ligand for this logic system (Supporting Information, Figure S12).

We finally investigated the effect of irradiation time with UV light. Photochemistry on a solid surface was different from that in solution,[13] thus the time required for isomerization for SP to MC on AuNP surface was not consistent with those in solutions. The spiropyran-AuNPs started to aggregate after 10 s of UV light irradiation, and the aggregation reached its maximum after a persistent irradiation for about 30 s, plateauing thereafter (Supporting Information, Figure S13), which is slower than that in solution (20 s; Supporting Information, Figure S1). This effect is probably due to the surface quenching and steric constraints of spiropyran on AuNP surface that decrease the isomerisation efficiency.[13c] The optimal irradiation time for spiropyran-AuNPs was thus about 30 s.

In conclusion, we have presented a spiropyran-AuNP-based, resettable, multi-readout logic system that includes AND, OR, and INHIBIT logic operations. The distinctive advantage of this system is that molecular events in aqueous solution could be translated into a color change of the solution, which can be monitored by several readouts, such as UV/Vis spectroscopy, zeta potential, DLS, and even the naked eye. Importantly, these logic gates were carried out in aqueous media, potentiating its applications in biological and biomedical systems.[14] Moreover, the set–reset function of these logic gates provides memory elements in an all-aqueous system, ensuring the entire operation is environmentally friendly. We believe that the combination of these logic gates with other novel technologies, such as lab-on-a-chip, could bring about a broad range of applications in analytical and material sciences.[15]

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