Articles

Multiple Logic Fluorescent Thermometer System Based on *N*-Isopropylmethacrylamide Copolymer Bearing Dicyanomethylene-4*H*-pyran Moiety

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ABSTRACT: The development of polymeric systems that can integrate individual basic logic gates into combinational circuits has been extremely interesting as smart materials. A novel thermometer fluorescent sensor poly(NIPMAM-*co*-MDCPDP) consisting of *N*-isopropylmethacrylamide (NIPMAM) as a thermoresponsive unit and dicyanomethylene-4*H*-pyran derivative as a dipolar-sensitive fluorophore unit was designed. Poly(NIPMAM-*co*-MDCPDP) performs fluorescence quenching merely by coordination with Cu^{2+} ions or increasing temperature in neutral or acid aqueous solution. The ON−OFF fluorescence response of poly(NIPMAM-*co*-MDCPDP) is driven by a temperature-induced phase transition from coil to globule and the capture of Cu^{2+} ions, resulting in a decrease of the ICT efficiency in neutral solution. The combinational serial NOR logic operation as well as two INHIBIT logic gates was constructed with three inputs: various pH, temperature change, and Cu^{2+} ions. The proposed combinational logic circuits play a key role in mimicking comprehensive arithmetic operations at the nanoscale level.

Introduction

The development of molecular systems that can integrate individual basic logic gates into combinational circuits has been extremely interesting as smart materials.[1,2] Many individual logic gates, such as AND, OR, NOT, XOR, XNOR, INHIBIT, and NOR, have been defined on the basis of spectral variations of molecular systems in response to external stimulations.[3] Particularly, the fluorescence signals to logic gates[4] have become a focus of considerable research due to their advantages such as high sensitivity, low background noises, and wide dynamic ranges. However, the inputs to fluorescent logic gates have almost been limited to chemical species such as ions or molecules. Thermosensitive polymers have attracted much research interest because of their technological importance and potentially biomedical applications.[5] Various fluorescent thermometers have also been studied extensively, which can be simple monitoring of solution temperature in the terms of emission intensity.[6] Previously, de Silva, Uchiyama, and Iwai et al. have reported the first realization of temperature as one of the inputs to AND logic gate based on a fluorescent *N*-alkyl-substituted polyacrylamide polymer.[5a] Considerably, polymeric materials consisting of ion sensing and thermosensitive moieties are expected to construct multiple logic gates.

Herein, we present a novel thermometer fluorescent sensor poly(NIPMAM-*co*-MDCPDP) consisting of *N*-isopropylmethacrylamide as a thermo-responsive unit and dicyanomethylene-4*H*-pyran derivative as a dipolar-sensitive fluorophore unit (Scheme 1). Poly(NIPMAM-*co*-MDCPDP) performs fluorescence quenching merely by coordination with Cu^{2+} ions or increasing temperature in neutral or acid aqueous solution. The specific responses of the copolymer to pH, metal cations, and temperature could provide three independent parameters that can be utilized to control the properties of the “smart” copolymer. Notably, the combinational serial NOR logic circuit as well as two INHIBIT logic gates was constructed with the three inputs of temperature, pH, and Cu^{2+} based on such “smart” copolymer.

Results and Discussion

Design and Synthesis. The fluorescent unit 2-{2-[4-(bis(pyridin-2-ylmethyl)amino)styryl]-6-[4-(piperazin-1-yl)styryl]-4*H*-pyran-4-ylidene}malononitrile (DCPDP) is depicted in Scheme 1. DCPDP was functionalized with methacryloyl chloride to gain the corresponding monomer MDCPDP. In ^1H NMR of DCPDP and MDCPDP, the characteristic coupling constant ($J = 16.0$ Hz) of alkene protons is indicative of the predominant *trans* isomer. Finally, poly(NIPMAM-*co*-MDCPDP) was prepared by free-radical copolymerization of MDCPDP and *N*-isopropylmethacrylamide (NIPMAM) in a solution of anhydrous tetrahydrofuran (THF) with 2,2-azobis(isobutyronitrile) (AIBN) as an initiator. The resulting molar ratio of DCPDP and NIPMAM units in the copolymer composition was 1:275, derived from ^1H NMR spectra or standard Job’s plot of MDCPDP absorption spectra in ethanol solution ($\xi = 29\,600$ M^{-1} cm^{-1} at 460 nm) (Supporting Information Figures S1−S3). Apparently, the molar ratio of MDCPDP units in the copolymer is much less than that of NIPMAM units so as not to distinctly affect the copolymeric thermosensitivity.

As a derivative of DCM (4-dicyanomethylene-2-methyl-6-[4-(dimethylamino)styryl]-4*H*-pyran),[7] the monomer of MDCPDP is also a typical donor-π-acceptor (D-π-A) structure with a broad absorption band resulting from an ultrafast process of intramolecular charge transfer (ICT).[8] Actually, the ICT mech-

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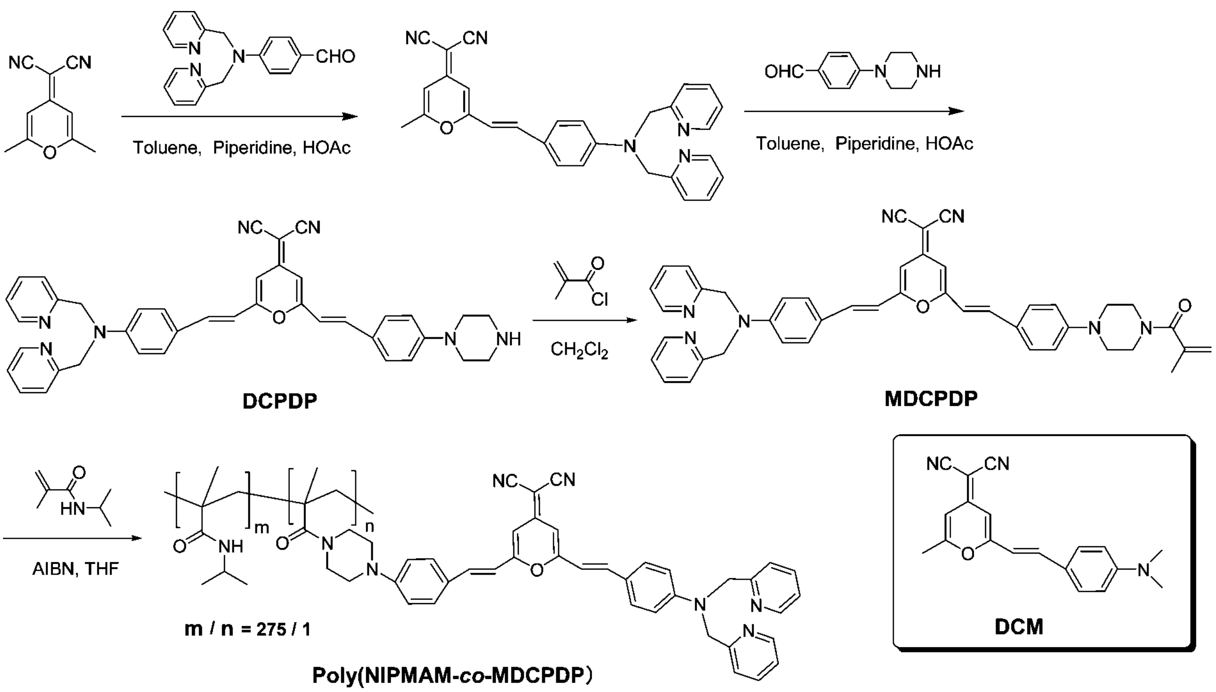
Scheme 1. Synthesis of Poly(NIPMAM-*co*-MDCPDP)



anism of DCM derivatives has been exploited for ion sensing and molecular switching, even for molecular logic gates.[9] Along with increasing solvent polarity, the dipole−dipole forces in the system of DCM derivatives become stronger, thus resulting in a larger charge transfer from the donor moiety of an amino group to the acceptor moiety of a dicyanomethylene group.[10] Consequently, the fluorescence quantum yield of MDCPDP is dramatically dependent upon solvent polarity. In addition, poly(*N*-isopropylacrylamide) (PNIPAM) is perhaps the most well-known member of thermoresponsiveness with a characteristic low critical solution temperature (LCST).[11] The homopolymer of *N*-isopropylmethacrylamide (NIPMAM) exhibits a coil-to-globule thermoreversible phase transition in dilute aqueous solution and has a LCST at about 46 °C.[11a,12] Taken into account in poly(NIPMAM-*co*-MDCPDP), the unit of NIPMAM is incorporated as a thermoresponsive function, labeled with the moiety of DCPDP as solvent polarity and ion sensing unit.

Thermoresponsive Behaviors and Ion Recognition. Since poly(NIPMAM) contains both hydrophilic amide groups and hydrophobic isopropyl groups on its side chains, most of the polar water molecules can be repelled out of the polymer when heating above the point of LCST,[5d] thus resulting in the characteristic thermosensitivity. Initially, the function of poly(NIPMAM-*co*-MDCPDP) as a fluorescence thermometer with pH condition was investigated in a mixture of water−ethanol (5:1, v/v) solution. Here we choose an ethanol−water mixture as solvent system based on the following considerations: (a) ethanol is a good solvent for PNIPMAM that polymer behaves as a flexible coil while the polymer is elongated and stiffer in pure water;[13a] (b) since the fluorescence of poly(NIPMAM-*co*-MDCPDP) becomes more quenched in pure water, we use an ethanol−water mixture as solvent system to make more distinct response to temperature and Cu^{2+}. As shown in Figure 1A, the occurrence of a LCST was distinctly observed during heating above 36 °C in a mixture of water−ethanol (5:1, v/v) solution at pH = 7, which is decreased by 10 °C than in aqueous solution due to the addition of ethanol.[13] Additionally, its fluorescent emission peak shows a hypsochromic shift by about 10 nm upon heating from 36 to 44 °C (Figure S4) due to the decreased microenvironmental polarity near DCPDP unit.[5a,d] Also as a result of the microenvironmental disturbance, the corresponding fluorescence is quenched to about 50% through a decrease in ICT efficiency[5a,6e] along with increasing temperature to 46 °C (Figure 2). More carefully, the fluorescence quenching was observed only in neutral and acidic conditions such as pH = 4

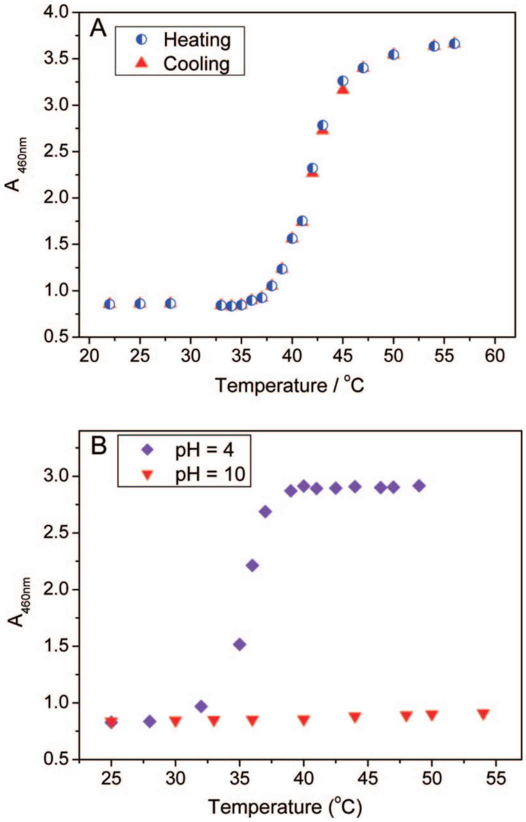


Figure 1. Temperature-dependent change in turbidity ($A_{460\ \mathrm{nm}}$) of poly(NIPMAM-*co*-MDCPDP) (1.6 g/L) in a mixture solution of water−ethanol (5:1, v/v): (A) at pH = 7; (B) at pH = 4 and pH = 10.

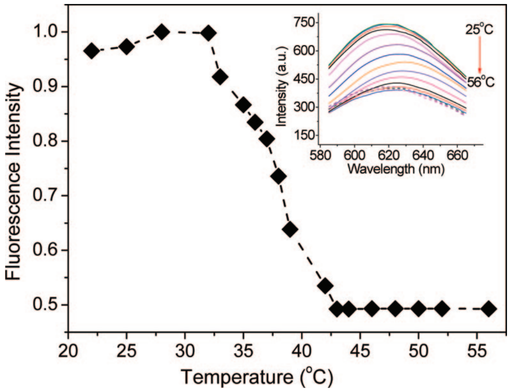


Figure 2. Fluorescence intensity−temperature diagram of poly(NIPMAM-*co*-MDCPDP) (1.6 g/L) in water−ethanol (5:1, v/v) solution at pH = 7 (λ_{ex} = 460 nm, λ_{em} = 620 nm). Inset: fluorescence spectra change with temperature at pH = 7.

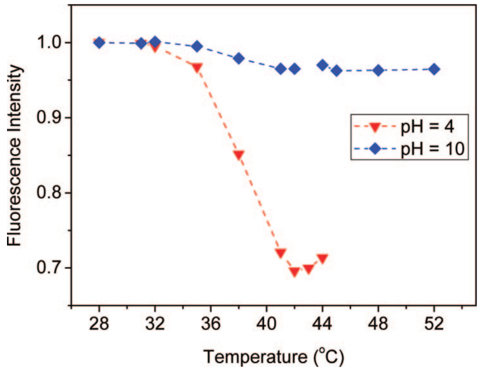


Figure 3. Fluorescence intensity−temperature characteristics of poly(NIPMAM-*co*-MDCPDP) (1.6 g/L) in a mixture of water−ethanol (5:1, v/v) solution at pH = 4 and pH = 10.

and slightly in alkaline conditions (pH = 10) with an increase of temperature (Figure 3). Also, the turbidity ($A_{460\ nm}$) curve of poly(NIPMAM-*co*-MDCPDP) increases drastically above 33 °C at pH = 4 due to the copolymer phase transition from coil to globule (Figure 1B). In contrast, at pH = 10, the absorbance of poly(NIPMAM-*co*-MDCPDP) at 460 nm does not show any obvious transition upon heating above 55 °C, suggestive of the less sensitivity of the copolymer to temperature in the alkaline environment (Figure 1B).[14] In addition, the emission intensity of monomer MDCPDP does not show obvious temperature-dependent change (Figure S5). Consequently, in the system of poly(NIPMAM-*co*-MDCPDP), the increase in the microenvironmental hydrophobicity of *N*-alkylacrylamide results in the high sensitivity toward the change in temperature at the pH range of 4.0−7.0 in that the copolymer thermosensitivity is dominated by the hydrophobicity/hydrophilicity balance of *N*-alkylacrylamide units.[14,15] Briefly, the pH change in the medium plays a key role in the ON−OFF switching for the fluorescent copolymeric thermometer.

As is well-known, bis(2-pyridylmethyl)amine (DPA) has been extensively used as a Zn^{2+} ligand owing to its high affinity and excellent selectivity.[16] Poly(NIPMAM-*co*-MDCPDP) should be candidate for ion chemosensor in that the MDCPDP monomer contains the DPA moiety. The selectivity and sensitivity of poly(NIPMAM-*co*-MDCPDP) were investigated with various metal ions in Figure 4. Other metal ions such as Na^+, Ag^+, Fe^{3+}, Fe^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} also show subtle disturbance, but only the addition of Cu^{2+} ions to poly(NIPMAM-*co*-MDCPDP) causes the significant decrease of fluorescence intensity acting as an efficient fluorescence quencher.[9b,17] It implies that the capture of Cu^{2+} ion by the receptor of DPA exhibits stronger binding affinity and decreases the electron-donating ability of the amino groups, thus resulting in a decrease of the ICT efficiency.[9b,16e] As reported previously, fluorescent sensors based on D-π-A type are usually disturbed by protons in the detection of metal ions.[18] Similarly, pH effect on the selectivity of poly(NIPMAM-*co*-MDCPDP) sensor shows that polymer only captures the Cu^{2+} ion in neutral and acid but not in base (Figures S6 and S7). With the increase of temperature at pH = 10, the fluorescent intensity exhibits a subtle change after the addition of 50 μM Cu^{2+} ions (Figure S6). Moreover, the quenching constant (K_{sv})[18] is determined to be about 1.06×10^5 M^{-1} by fluorometric titration curves as the nonlinear decrease of fluorescence intensity with the addition of Cu^{2+} ions in a mixture solution of water−ethanol (5:1, v/v) at pH = 7 (Figure 5).

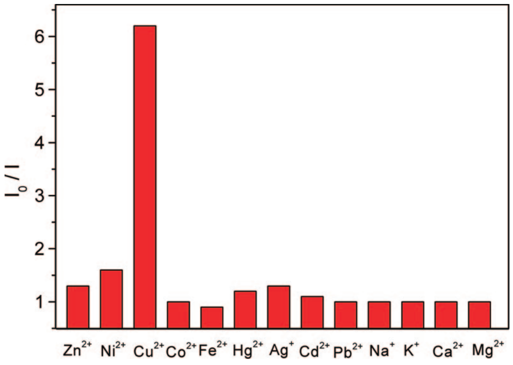


Figure 4. Fluorescence intensity change of poly(NIPMAM-*co*-MDCPDP) (1.6 g/L) in a mixture solution of water−ethanol (5:1, v/v) at pH = 7 in the presence of various metal ions (0.2 mM, λ_{ex} = 505 nm, λ_{em} = 620 nm). Note: I_0/I represents the ratio of the fluorescence intensity change before and after the addition of various metal ions with poly(NIPMAM-*co*-MDCPDP).

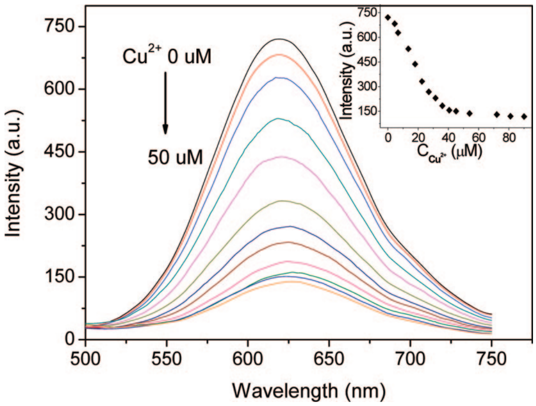
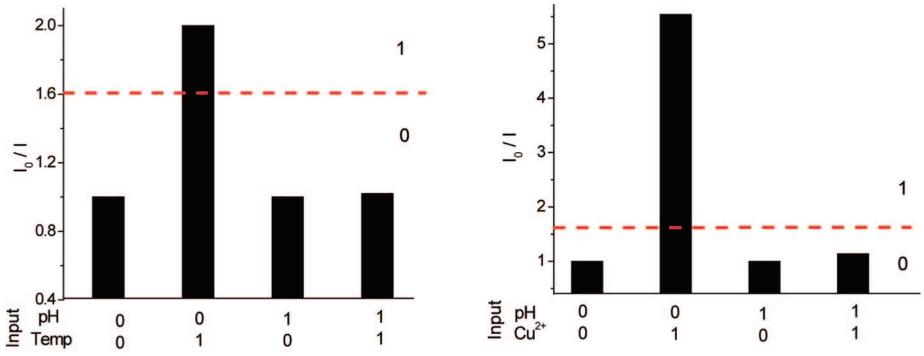


Figure 5. Emission spectra of poly(NIPMAM-*co*-MDCPDP) (1.6 g/L) upon titration with Cu^{2+} ions from 0 to 50 μM in a mixture of water−ethanol (5:1, v/v) solution at pH = 7. Inset: fluorescence intensity at λ_{em} = 620 nm as a function of Cu^{2+} concentration.

Combinational Logic Function. To take advantage of the ON−OFF fluorescence response of poly(NIPMAM-*co*-MDCPDP) driven by a temperature-induced phase transition from coil to globule and the capture of Cu^{2+} ions resulting in a decrease of the ICT efficiency in neutral solution, the combinational serial NOR logic operation as well as two INHIBIT logic gates was constructed with pH as an input and either Cu^{2+} ions or temperature as another input. An INHIBIT logic gate is a two-input AND gate with one input carrying a NOT gate. The values of I_0/I at 620 nm of poly(NIPMAM-*co*-MDCPDP) to the different combinations of varying temperature and pH correspond to an INHIBIT logic gate. The four situations are examined (Figure 6c), in which pH as input 1 is 10 (high, 1) or



a b

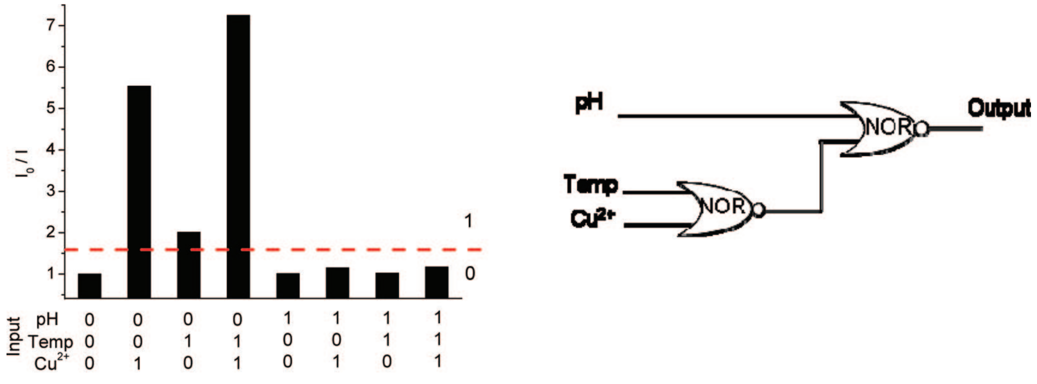
Input1 (pH)	Input2 (Temp.)	Output (I_0/I)
0	0	0 (1.00)
0	1	1 (2.01)
1	0	0 (1.01)
1	1	0 (1.02)

c

Input1 (pH)	Input2 (Cu^{2+})	Output (I_0/I)
0	0	0 (1.00)
0	1	1 (5.54)
1	0	0 (1.01)
1	1	0 (1.15)

d

Figure 6. Two INHIBIT logic gates constructed with pH as an input and either Cu^{2+} ions or temperature as another input (the threshold is 1.6). The values of I_0/I at 620 nm as the output of the INHIBIT gate from the different inputs: (a) pH and temperature; (b) pH and Cu^{2+}; Truth tables (c, d) of two INHIBIT gates.



a b

Figure 7. Combinational logic operation. (a) The values of I_0/I at 620 nm as the output of the combinational logic operation at 620 nm from the eight possible inputs. (b) The corresponding physical electronic symbols of combinational logic circuit.

7 (low, 0) and temperature as input 2 is 46 °C (high, 1) or 25 °C (low, 0). As shown in Figure 6a, the value of I_0/I at 620 nm (output) becomes distinctly high ($I_0/I = 2.01$) only when the temperature reaches 46 °C at pH = 7. In contrast, the values of I_0/I hold a low level ($I_0/I < 1.60$) at the other three situations. Similarly, the different input combinations of adding Cu^{2+} ions and varying pH for poly(NIPMAM-*co*-MDCPDP) are also constructed as an INHIBIT logic gate with the values of I_0/I (620 nm) as the output. The observations are complied with the INHIBIT gate function and presented in Truth table (Figure 6b,d). In this INHIBIT logic gate, pH as input 1 is 10 (high, 1) or 7 (low, 0) and the addition of Cu^{2+} ions as input 2 is 50 μM (high, 1).

Generally, the combinational logic circuits play a key role in mimicking comprehensive arithmetic operations at the molecular or nanoscale level.[1a] A combinational serial NOR logic operation can be constructed with three inputs: various pH, temperature change, and Cu^{2+} ions (Figure 7b). The NOR logic operation is an integration of NOT and an OR logic gate, in which the output is low when one or more of the inputs are high. The eight possible input combinations of varying pH, temperature, and Cu^{2+} ions are shown in Figure 7a. Obviously, the values of I_0/I at 620 nm are hold high ($I_0/I > 1.60$) when either Cu^{2+} or temperature inputs or both above two inputs are "1" at pH = 7 (Figure 7 and Figure S8). The output signals of other five combinational input situations are hold low. Notably, all above logic operations at the threshold 1.6 can be reset, simply by adding the equivalent of acid at pH = 10 and a more competitive chelator such as ethylenediaminetetraacetic acid (EDTA).

Conclusions

A smart copolymer of poly(NIPMAM-*co*-MDCPDP) derived from dicyanomethylene-4*H*-pyran chromophore has been designed for logic fluorescent thermometer system based on the hydrophobicity/hydrophilicity balance of copolymer chain and ions sensing. Poly(NIPMAM-*co*-MDCPDP) displays the specific ON−OFF fluorescence signals only upon adding Cu^{2+} or increasing temperature in neutral or acid solution. Two INHIBIT logic gates were constructed with pH as one input and either Cu^{2+} or temperature as another input. Similarly, the combinational serial NOR logic operation was also implemented by the different combination of three inputs: temperature, Cu^{2+} ions, and pH. The proposed combinational logic circuits play a key role in mimicking comprehensive arithmetic operations at the nanoscale level. Moreover, for the device strategy, the thin film prototype based on the similar cross-linker copolymer is undergoing in our laboratory. A possible way implements the above continuous operations to immobilize the copolymer on a solid substrate and to carry out the experiment in a flow cell. The multiple logic fluorescent thermometer system might be contributed to the development of more smart fluorescent materials, which makes more attractive for future developments such as microgel assembly, drug-controlled release, and optical and rheological applications.

Experimental Section

All solvents were of analytical grade. The intermediates of 2,6-dimethyl-4-dicyanomethylene-4*H*-pyran and 4-[bis(pyridin-2-ylmethyl)amino]benzaldehyde were prepared by the established literature procedures.[19,20] ^1H NMR and ^{13}C NMR in $CDCl_3$ or DMSO-d_6 were measured on a Bruker AV-400 or AV-500 spectrometer with tetramethylsilane (TMS) as internal standard. Mass spectra were measured on a Micromass LCT. UV−vis spectra were obtained using a Varian Cary 500 spectrophotometer (1 cm quartz cell). Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell). The measurements took place in the temperature range from 20 to 55 °C with a heating/cooling rate of 1 °C/min. The pH value was checked by pHS-25 with a range from pH 0−14. The weight-average molecular weights (M_n) and polydispersity (M_w/M_n) of the polymer were measured by GPC (Waters 1515/Wyatt Technology Corp.) at 30 °C using THF as eluent and standard polystyrene as the reference.

2-{2-[4-(Bis(pyridin-2-ylmethyl)amino)styryl]-6-methyl-4*H*-pyran-4-ylidene}malononitrile. The treatment of 2,6-dimethyl-4-dicyanomethylene-4*H*-pyran (0.5 g, 2.9 mmol) and 4-[bis(pyridin-2-ylmethyl)amino]benzaldehyde (0.7 g, 2.2 mmol) in the presence of acetic acid, piperidine, and toluene with concomitant removal of water was refluxed for about 5 h. The solvent was evaporated in vacuo. The crude solid was purified by column chromatography on silica gel eluting with EtOAc to afford a purple solid in 55% yield. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.99 (s, 3H, $-CH_3$), 4.89 (s, 4H, $-N-CH_2-$), 6.44 (d, 1H, $J = 16.0$ Hz, alkene-H), 6.49 (d, 1H, $J = 2.0$ Hz, pyran-H), 6.57 (d, 1H, $J = 2.0$ Hz, pyran-H), 6.74 (d, 2H, $J = 8.8$ Hz, phenyl-H), 7.21 (m, 2H, pyridine-H), 7.25 (d, 2H, $J = 6.1$ Hz, pyridine-H), 7.32 (d, 1H, $J = 16.0$ Hz, alkene-H), 7.35 (d, 2H, $J = 8.8$ Hz, phenyl-H), 7.64 (t × d, 2H, $J = 7.7$, 1.6 Hz, pyridine-H), 8.62 (d, 2H, $J = 4.7$ Hz, pyridine-H).

2-{2-[4-(Bis(pyridin-2-ylmethyl)amino)styryl]-6-[4-(piperazin-1-yl)styryl]-4*H*-pyran-4-ylidene}malononitrile (DCPDP). 2-(2-(4-(Bis(pyridin-2-ylmethyl)amino)styryl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile (0.457 g, 1.0 mmol) and 4-(piperazin-1-yl)benzaldehyde (0.26 g, 1.3 mmol) were dissolved in toluene (50 mL) with piperidine (0.4 mL) and acetic acid (0.8 mL) under argon protection at room temperature. Then the mixture was refluxed and stirred for 8 h. The solvent was evaporated in vacuo. The crude solid was purified by column chromatography on silica gel eluting with ethanol to afford a purple solid in 35% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.04 (t, 4H, $J = 5.0$ Hz, piperazine-H), 3.29 (t, 4H, $J = 5.0$ Hz, piperazine-H), 4.91 (s, 4H, $-N-CH_2-$), 6.50 (d, 1H, $J = 16.0$ Hz, alkene-H), 6.56 (d, 1H, $J = 16.0$ Hz, alkene-H), 6.57 (d, 1H, $J = 2.0$ Hz, pyran-H), 6.58 (d, 1H, $J = 2.0$ Hz, pyran-H), 6.74 (d, 2H, $J = 8.8$ Hz, phenyl-H), 6.91 (d, 2H, $J = 8.8$ Hz, phenyl-H), 7.21 (m, 2H, pyridine-H), 7.25 (d, 2H, $J = 8.0$ Hz, pyridine-H), 7.40 (d, 2H, $J = 8.6$ Hz, phenyl-H), 7.41 (d, 1H, $J = 16.0$ Hz, alkene-H), 7.44 (d, 1H, $J = 16.0$ Hz, alkene-H), 7.46 (d, 2H, $J = 8.8$ Hz, phenyl-H), 7.67 (t, 2H, $J = 7.5$ Hz, pyridine-H), 8.62 (d, 2H, $J = 4.7$ Hz, pyridine-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 44.34, 45.20, 48.24, 57.17, 105.63, 105.90, 112.79, 113.81, 114.85, 115.07, 115.94, 120.82, 122.38, 123.72, 125.29, 129.35, 129.72, 137.00, 137.60, 137.95, 149.85, 150.15, 152.57, 156.00, 157.77, 158.86, 159.10.

2-{2-[4-(4-Methacryloylpiperazin-1-yl)styryl]-6-[4-(bis(pyridin-2-ylmethyl)amino)styryl]-4*H*-pyran-4-ylidene}malononitrile (MDCPDP). DCPDP (125 mg, 0.19 mmol) and methacryloyl chloride (60 mg, 0.6 mmol) were both dissolved in CH_2Cl_2 (20 mL) with triethylamine (0.5 mL) under argon protection at room temperature for 24 h. Then the solvent was evaporated in vacuo. The crude solid was purified by column chromatography on silica gel eluting with EtOAc:CH_2Cl_2 = 1:1 to afford a purple solid in 67% yield. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.99 (s, 3H, $-CH_3$), 3.31 (t, 4H, $J = 5.0$ Hz, piperazine-H), 3.77 (t, 4H, $J = 5.0$ Hz, piperazine-H), 4.91 (s, 4H, $-NCH_2-$), 5.09 (s, 1H, $-C{=}CH_2$), 5.26 (s, 1H, $-C{=}CH_2$), 6.50 (d, 1H, $J = 16.0$ Hz, alkene-H), 6.57 (d, 1H, $J = 2.0$ Hz, pyran-H), 6.58 (d, 1H, $J = 16.0$ Hz, alkene-H), 6.59 (d, 1H, $J = 2.0$ Hz, pyran-H), 6.77 (d, 2H, $J = 8.8$ Hz, phenyl-H), 6.92 (d, 2H, $J = 8.8$ Hz, phenyl-H), 7.22 (m, 2H, pyridine-H), 7.25 (d, 2H, $J = 8.0$ Hz, pyridine-H), 7.40 (d, 1 H, $J = 16.0$ Hz, alkene-H), 7.41 (d, 2H, $J = 8.6$ Hz, phenyl-H), 7.42 (d, 1H, $J = 16.0$ Hz, alkene-H), 7.48 (d, 2H, $J = 8.8$ Hz, phenyl-H), 7.66 (t × d, 2H, $J = 7.7$ Hz, 1.6 Hz, pyridine-H), 8.63 (d, 2H, $J = 4.4$ Hz, pyridine-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 20.50, 48.22, 48.73, 57.22, 57.50, 105.67, 106.12, 112.82, 113.82, 115.41, 115.57, 115.87, 116.00, 120.82, 122.39, 123.72, 125.97, 129.35, 129.73, 136.99, 137.36, 138.01, 140.08, 149.90, 150.20, 152.03, 156.00, 157.79, 158.69, 159.18, 171.26. HRMS: $C_{44}H_{39}N_7O_2$ (ESI positive ion mode for M + H): Calculated, 698.3271; Found, 698.3243 (ESI positive ion mode for M + Na): Calculated, 720.3034; Found, 720.3063 (100%).

Poly(NIPMAM$_m$-*co*-MDCPDP$_n$) (m/n = 275/1). The *N*-isopropylmethacrylamide monomer (1.13 g, 9 mmol), MDCPDP monomer (63 mg, 0.09 mmol), and the initiator α,α'-azoisobutyronitrile (AIBN; 10 mg, 0.06 mmol) were dissolved in anhydrous THF (10 mL). After this the mixture was shaken for 5 min at ambient temperature, and the reaction mixture was degassed by subjecting it to freeze−thaw cycle three times. After being heated for 2 days at 65 °C, the resultant mixture was poured into ether and precipitated with ether four times and then filtrated. The resulting copolymer was dried in vacuum to give a slight red powder. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 0.8−1.16 (m, $-CH(CH_3)_2$, $-CH_3$), 1.6 (br, $-CCH_2$), 2.90 (br, piperazine-H), 3.10 (br, piperazine-H), 3.77 (br, 1H, $-NH-CH-$), 4.93 (br, $-N(CH_2)-$), 6.80 (br, $-NH-CH$), 7.10−7.75 (br, weak aromatic and pyridine H), 8.60 (br, 2H). GPC (THF): M_n = 7026, M_w = 9246, M_p = 8542, M_w/M_n = 1.31.

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Supporting Information Available: Structure characterization of poly(NIPMAM-*co*-MDCPDP); absorption and fluorescence spectra with varying temperature, Cu^{2+} ions, and pH. This material is available free of charge via the Internet at http://pubs.acs.org.

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References and Notes

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