A fluorescent acrylamide-type monomer bearing an environment-sensitive methoxybenzocoumarin structure for the development of functional polymeric sensors†

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A new fluorescent acrylamide-type monomer bearing a hydrogen bonding- and polarity-sensitive benzo-coumarin fluorophore was synthesized. The absorption spectra, fluorescence spectra, and fluorescence lifetime of a model compound were measured in ten solvents with different hydrogen-bonding abilities and polarities to investigate the sensitivity of the fluorophore to the surrounding environment. These spectroscopic studies demonstrated that the fluorophore emits stronger fluorescence in more protic, polar environments. A fluorescent polymeric thermometer was prepared from N-isopropylacrylamide and the new fluorescent monomer, and it showed good functionality in aqueous solution (e.g., high sensitivity to temperature changes and high chemical stability), indicating the applicability of the herein developed fluorescent monomer for use in functional sensors.

Introduction

Environment-sensitive fluorophores change their photophysical properties (e.g., fluorescence quantum yield, maximum emission wavelength, and fluorescence lifetime) depending on the surrounding environment. Fluorescent monomers consisting of an environment-sensitive fluorophore and a polymerizable vinyl bond are valuable in polymer chemistry because they can facilitate the elucidation of the microenvironments of macromolecules and the development of functional polymeric materials with applications in a wide range of scientific disciplines. Examples of the latter case include fluorescent monomers bearing an environment-sensitive dansyl, benzofurazan, aminocoumarin, or naphthalimide fluorophore, which have been used to construct fluorescent polymeric thermometers by us and other groups. Intracellular thermometry can now be performed with these fluorescent polymeric thermometers. Fluorescent polymeric sensors for potassium ions, sulfate ions, phosphatidyl-inositol-4,5-bisphosphate, and phosphatidylserine are also examples of macromolecular materials created from fluorescent monomers containing an environment-sensitive fluorophore. The use of some of these sensors has been explored to monitor biologically important molecules in live cell imaging. It should be noted that all of the fluorescent monomers in the functional polymers described above bear an environment-sensitive fluorophore, which shows stronger fluorescence in less protic, polar environments (e.g., in an aprotic organic solvent, such as ethyl acetate). Fluorescent monomers containing a fluorophore with the opposite sensitivity to the environment, i.e., those that emit stronger fluorescence in more protic, polar environments, are worthwhile components for the development of functional polymers with new properties.

In our previous study, we found that 8-methoxy-4-methyl-2H-benzo[g]chromen-2-one (MBC) (Fig. 1) is an environment-sensitive fluorophore that emits stronger fluorescence in more protic, polar environments. The unique fluorescent monomer (8-methoxy-2-oxo-2H-benzo[g]chromen-4-yl)methyl acrylate (MBC-AE), which bears the MBC structure, was synthesized, and a fluorescent polymeric thermometer, poly(N-isopropylacrylamide-co-MBC-AE) (poly(NIPAM-co-MBC-AE)) was prepared as an example of the use of this monomer. Poly(NIPAM-co-MBC-AE) showed temperature-dependent fluorescence in aqueous solution because the microenvironment near the MBC-AE units was changed by the thermo-responsive behavior of the polyNIPAM units. Nevertheless, the repeatable thermo-responsive function of poly(NIPAM-co-MBC-AE) was observed only under acidic conditions because the MBC-AE units in poly(NIPAM-co-MBC-AE) were hydrolyzed under neutral and basic conditions.
To address this shortcoming, herein, we synthesized \( N-((8\text{-methoxy-2-oxo-2H-benzo}[g]\text{chromen-4-yl})\text{-methyl})\text{-N-methyl-acrylamide (MBC-AA)} \) as a new acrylamide-type fluorescent monomer. The amide-type MBC-AA unit was expected to be more tolerant to hydrolysis than the ester-type MBC-AE unit when introduced into a polymer. \( N-((8\text{-methoxy-2-oxo-2H-benzo}[g]\text{chromen-4-yl})\text{-methyl})\text{-N-methyisobutylamide (MBC-IA)} \) was also synthesized as a model compound of the MBC-AA unit. The fluorescence properties of MBC-IA were investigated in ten solvents to determine the sensitivity of the fluorophore to the surrounding environment. In addition, poly(NIPAM-co-MBC-AA) was prepared, and its fluorescence properties were studied. The utility of the new fluorescent monomer MBC-AA was assessed by investigating the thermo-responsive function of poly(NIPAM-co-MBC-AA) in water.

**Experimental**

**Materials and apparatus**

Poly[NIPAM-co-MBC-AE] (weight-average molecular weight \( M_w = 148\,000 \), number-average molecular weight \( M_n = 51\,500 \), \( M_w/M_n = 2.87 \)) was obtained as previously reported.\(^{14}\) \(^1\)H NMR spectra were recorded using a Bruker Avance 400 spectrometer. The mass spectra acquired via electrospray ionization (ESI) were recorded using a Bruker microTOF-05 spectrometer. The melting points were measured using a Round Science RFS-10 and are uncorrected. The gel-permeation chromatography (GPC) equipment consisted of a JASCO PU-2080 pump, a Jasco RI-2031 refractive index detector, a JASCO FP-2020 fluorescence detector, a JASCO CO-2060 column thermostat, and a Shodex GPC KD-806 M column. A calibration curve was obtained using polystyrene standards, and 1-methyl-2-pyrrolidinone containing LiBr (5 mM) was used as the eluent.

**Synthesis**

8-Methoxy-4-((methylamino)methyl)-2H-benzo[g]chromen-2-one (MBC-MA). 4-Chloromethyl-8-methoxy-2H-benzo[g]chromen-2-one (100 mg, 0.36 mmol)\(^{14}\) was dissolved in acetonitrile (20 mL). After the addition of 40% methylene solution (607 \( \mu L, 7.0 \) mmol), the mixture was stirred at 50 °C for 3 h. Then, the reaction mixture was evaporated to dryness under reduced pressure, and the residue was separated by chromatography on silica gel using dichloromethane–methanol (95 : 5, \( \nu/\nu \)) to afford MBC-MA (21.2 mg, 22%) as a pale yellow powder: mp, 132–133 °C; \(^1\)H NMR (CDCl\(_3\))\( \delta \) 8.01 (1H, s), 7.76 (1H, \( d, J = 9.0 \) Hz), 7.51 (1H, s), 7.11 (1H, \( dd, J = 9.0, 2.2 \) Hz), 7.03 (1H, \( d, J = 2.2 \) Hz), 6.48 (1H, s), 4.00 (2H, s), 3.93 (3H, s), 2.58 (3H, s); \(^1\)C NMR (CDCl\(_3\))\( \delta \) 161.8, 160.2, 153.6, 151.7, 136.9, 130.8, 126.2, 124.6, 120.1, 117.0, 113.6, 112.4, 105.1, 56.0, 52.2, 37.1. High-resolution ESI mass spectrometry (HR-ESI-MS): \( m/z \) Calcd for \( C_{16}H_{16}NO_4^+ [M + H]^+ \) 270.1125. Found 270.1125.

MBC-AA. MBC-MA (70 mg, 0.26 mmol) was dissolved in acetonitrile (10 mL). After the addition of triethylamine (36.2 \( \mu L, 0.26 \) mmol) and acryloyl chloride (82.2 \( \mu L, 1.02 \) mmol), the mixture was stirred at 50 °C for 4.5 h. Then, \( \text{Na}_2\text{CO}_3 \) (1 g) was added to the solution to stop the reaction. After filtration to remove excess \( \text{Na}_2\text{CO}_3 \), the reaction mixture was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel using dichloromethane–methylol (50 : 1, \( \nu/\nu \)) to afford MBC-AA (69.0 mg, 72%) as a yellow powder: mp, 166–167 °C; \(^1\)H NMR (CDCl\(_3\))\( \delta \) 8.04, 7.91 (1H, s), 7.77 (1H, \( d, J = 9.2 \) Hz), 7.58, 7.55 (1H, s), 7.11–7.18 (1H, m), 7.07 (1H, s), 6.43–6.73 (2H, m), 6.24, 6.17 (1H, s), 5.69–5.84 (1H, m), 4.91, 4.87 (2H, s), 3.94 (3H, s), 3.16 (3H, s); \(^1\)C NMR (CDCl\(_3\))\( \delta \) 166.7, 160.6, 159.7, 150.7, 150.0, 136.4, 130.3, 130.0, 129.5, 126.7, 125.5, 124.2, 123.0, 119.7, 119.5, 115.5, 112.6, 112.0, 111.7, 104.5, 55.4, 53.4, 50.1, 48.0, 35.7, 35.0, 29.6, 23.3. HR-ESI-MS: \( m/z \) Calcd for \( C_{20}H_{16}N_2O_4Na^+ [M + Na]^+ \) 346.1050. Found 346.1055.

MBC-IA. MBC-MA (20 mg, 0.074 mmol) was dissolved in acetonitrile (3 mL). After the addition of triethylamine (13.5 \( \mu L, 0.097 \) mmol) and isobutynic anhydride (16.1 \( \mu L, 0.097 \) mmol), the mixture was stirred at room temperature for 4 h. Then \( \text{K}_2\text{CO}_3 \) (1 g) was added to the solution to stop the reaction. After filtration to remove excess \( \text{K}_2\text{CO}_3 \), the reaction...
mixture was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel using dichloromethane–methanol (50:1, v/v) to afford MBC-IA (19.3 mg, 77%) as a yellow powder: mp, 188–190 °C; 1H NMR (CDCl3) δ 8.05, 7.93 (1H, s), 7.76–7.81 (1H, m), 7.64, 7.59 (1H, s), 7.09–7.18 (2H, m), 6.22, 6.17 (1H, s), 4.87, 4.84 (2H, s), 3.98, 3.95 (3H, s), 3.11, 3.09 (3H, s), 2.61–2.97 (m, 1H), 1.17–1.22 (6H, m); 13C NMR (CDCl3) δ 177.4, 160.8, 159.7, 150.9, 150.7, 136.5, 130.4, 125.6, 124.5, 119.6, 115.7, 113.1, 111.8, 104.5, 55.4, 47.9, 35.2, 30.5, 29.7, 19.2. HR-ESI-MS: m/z Calcd for C26H31N2O3; [M + Na]+ 362.1368. Found 362.1363.

Poly(NIPAM-co-MBC-AA). NIPAM (2.5 mmol), MBC-AA (2.5 μmol), and α,α’-azobisisobutyronitrile (25 μmol) were dissolved in 1,4-dioxane (5 mL), and the solution was bubbled with dry Ar for 30 min to remove dissolved oxygen. The solution was heated at 60 °C for 6 h and then cooled to room temperature. The reaction mixture was then poured into diethyl ether (100 mL) (yield: 76%). The proportion of MBC-AAA in the copolymer was determined by comparing the absorbance in methanol with that of the model fluorophore MBC-IA. The molecular weights ($M_w$ and $M_n$) were determined by GPC with a refractive index detector.

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**Results and discussion**

**Synthesis of MBC-IA and MBC-IA**

The new fluorescent monomer MBC-AA and the model compound MBC-IA were synthesized from 4-chloromethyl-8-methoxy-2H-benzochromen-2-one by two-step reactions (Fig. 2). In the first reaction, the methylen amino group was introduced by nucleophilic substitution under mild conditions.

$$I(t) = \sum_{i=1}^{n} B_i \exp\left(-\frac{t}{\tau_i}\right)$$

Then, the $\tau_i$ values were calculated using eqn (3).

$$\tau_i = \frac{\sum_{i=1}^{n} B_i \tau_i^2}{\sum_{i=1}^{n} B_i \tau_i}$$

The fractional contributions ($P_i$ for $\tau_i$) were calculated using eqn (4).

$$P_i = 100 \times \frac{B_i \tau_i}{\sum_{i=1}^{n} B_i \tau_i}$$

**Functional studies of poly(NIPAM-co-MBC-AA)**

The fluorescence spectra of poly(NIPAM-co-MBC-AA) (0.01% w/v) were recorded in 1,4-dioxane, acetonitrile, ethanol, methanol, and water with excitation at 345 nm. After ten cycles of heating (to 45 °C) and cooling (to 25 °C) in water, the polymer solution was lyophilized, and the residue was redissolved in 1-methyl-2-pyrrolidinone (0.5% w/v) for subsequent GPC. The hydrodynamic diameter of poly(NIPAM-co-MBC-AA) was estimated from dynamic light scattering (DLS) measurements using a Zetasizer Nano ZS (Malvern Instruments). The samples (0.01% w/v) were equilibrated at 20 °C for 10 min.

$$\Phi_i = 0.26$$

$$\tau_i = \frac{\sum_{i=1}^{n} B_i \tau_i^2}{\sum_{i=1}^{n} B_i \tau_i}$$

$$P_i = 100 \times \frac{B_i \tau_i}{\sum_{i=1}^{n} B_i \tau_i}$$

$$k_f = \frac{\Phi_i}{\tau_i}$$

$$k_{nr} = 1 - \frac{\Phi_i}{\tau_i}$$

**Fig. 2.** Synthesis of MBC-AA and MBC-IA. (i) 40% MeNH$_2$, MeCN, 50 °C, 3 h (22%); (ii) acryloyl chloride, Et$_3$N, MeCN, 50 °C, 4.5 h (72%); and (iii) isobutyric anhydride, Et$_3$N, MeCN, rt, 4 h (77%).
Then, acylation was performed using acryloyl chloride and iso-butyric anhydride to obtain MBC-IA and MBC-AA, respectively.

**Fluorescence properties of MBC-IA**

The absorption and fluorescence spectra of the model fluorophore MBC-IA were recorded in ten solvents (n-hexane, 1,4-dioxane, ethyl acetate, acetonitrile, chloroform, ethanol, methanol, a mixture of water and methanol [4:1, v/v], water, and trifluoroethanol) (Fig. 3). Table 1 summarizes the photophysical properties of MBC-IA in these solvents and the solvents’ hydrogen-bonding ability (*i.e.*, hydrogen-bond donor acidity α (ref. 16)) and polarity (*i.e.*, dielectric constant *D* (ref. 17)). Similar to MBC, although MBC-IA was almost non-fluorescent in aprotic, apolar solvents (*e.g.*, Φ<sub>f</sub> = 0.0054 in n-hexane), it strongly fluoresced in protic, polar solvents (*e.g.*, Φ<sub>f</sub> = 0.35 in methanol).

Regarding the maximum emission wavelength, MBC-IA fluoresced at longer wavelengths as the hydrogen-bonding ability and polarity of the solvent increased, indicating that the first singlet state of MBC-IA has an intramolecular charge transfer (ICT) character. Table 1 also shows the fluorescence lifetimes (see Fig. S1† for the original fluorescence decay curves), fluorescence rate constants, and non-radiative rate constants of MBC-IA in the different solvents. The high efficiency of the non-radiative relaxation process in MBC-IA in aprotic, apolar solvents is because of the proximity of an emissive π*π* state to a non-emissive ππ* state. Comparing the photophysical properties of MBC-IA in acetonitrile (Φ<sub>f</sub> = 0.031, hydrogen-bond donor acidity α = 0.19 and dielectric constant *D* = 37.5) and in methanol (Φ<sub>f</sub> = 0.35, α = 0.93, and *D* = 32.6) revealed that the fluorescence process of MBC-IA is dominantly influenced by the hydrogen-bonding ability of the solvent rather than by its polarity. The non-radiative process of MBC-IA in water was accelerated compared to that in methanol, although water has a stronger hydrogen-bonding ability (*α* = 1.17) than methanol (*α* = 0.93). The proximity of the first singlet ππ* state to the ground state in more polar environments, as indicated by the longer emission wavelength (*i.e.*, 540 nm in water), increases the efficiency of the non-radiative internal conversion. This effect has been established as the “energy gap law”<sup>20</sup> in photochemistry. It should be also noted that the fluorescence rate constant of MBC-IA was strongly influenced by the solvents (see Table 1). Because such a decrease in the *k<sub>f</sub>* value in the non-polar solvents (*i.e.*, n-hexane, 1,4-dioxane and ethyl acetate) was not observed in the original fluorophore MBC,<sup>19</sup> the dependency of the *k<sub>f</sub>*

![Absorption (black line) and fluorescence (red line) spectra of MBC-IA (10 μM) in various solvents at 25 °C. All fluorescence spectra were recorded with excitation at the maximum absorption wavelength.](image)

**Table 1** Photophysical properties of MBC-IA: fluorescence quantum yield (Φ<sub>f</sub>), maximum absorption wavelength (λ<sub>abs</sub>), molar absorption coefficient (ε), maximum emission wavelength (λ<sub>em</sub>), fluorescence lifetime (*τ*<sub>f</sub>), fluorescence rate constant (*k<sub>f</sub>*), and non-radiative rate constant (*k<sub>nr</sub>*)

| Solvent                  | α<sup>a</sup> | *D*<sup>b</sup> | Φ<sub>f</sub> | λ<sub>abs</sub>/nm | ε/cm<sup>−1</sup>*M<sup>−1</sup> | λ<sub>em</sub>/nm | *τ*<sub>f</sub>/ns | *k<sub>f</sub>/10<sup>7</sup> s<sup>−1</sup> | *k<sub>nr</sub>/10<sup>7</sup> s<sup>−1</sup> |
|-------------------------|---------------|-----------------|---------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| n-Hexane                | 0.00          | 1.9             | 0.0054        | 342                 | 1600            | 425             | 0.98            | 0.55            | 100             |
| 1,4-Dioxane             | 0.00          | 2.2             | 0.0033        | 343                 | 1600            | 462             | 0.86            | 0.38            | 116             |
| Ethyl acetate           | 0.00          | 6.0             | 0.0053        | 342                 | 15500           | 432             | 1.1             | 0.47            | 87              |
| Acetonitrile            | 0.19          | 37.5            | 0.031         | 343                 | 15200           | 483             | 2.7<sup>d</sup> | 1.1             | 35              |
| Chloroform              | 0.44          | 4.8             | 0.052         | 349                 | 16400           | 468             | 3.0<sup>e</sup> | 1.7             | 32              |
| Ethanol                 | 0.63          | 24.3            | 0.26          | 347                 | 15600           | 502             | 5.2             | 4.9             | 14              |
| Methanol                | 0.93          | 32.6            | 0.35          | 346                 | 14900           | 512             | 6.3             | 5.5             | 10              |
| Water-methanol [4 : 1, v/v] | 0.70         | 70.7            | 0.28          | 348                 | 14400           | 540             | 4.4             | 6.3             | 16              |
| Water                   | 1.17          | 78.5            | 0.17          | 346                 | 13100           | 540             | 3.4             | 5.1             | 24              |
| Trifluoroethanol        | 1.51          | 26.8            | 0.33          | 349                 | 15600           | 538             | 6.0             | 5.4             | 11              |

<sup>a</sup> Hydrogen-bond donor acidity of the solvent.<sup>16</sup>  
<sup>b</sup> Dielectric constant of the solvent.<sup>17</sup>  
<sup>c</sup> Average fluorescence lifetime of three components: *τ*<sub>1</sub> = 0.21 ns (45%), *τ*<sub>2</sub> = 1.1 ns (51%), and *τ*<sub>3</sub> = 5.0 ns (3.7%).  
<sup>d</sup> Average fluorescence lifetime of two components: *τ*<sub>1</sub> = 0.63 ns (53%) and *τ*<sub>2</sub> = 5.1 ns (47%).  
<sup>e</sup> Average fluorescence lifetime of two components: *τ*<sub>1</sub> = 1.2 ns (69%) and *τ*<sub>2</sub> = 7.0 ns (31%).
values of MBC-IA on the solvents can be ascribed to the interaction of the fluorophore (i.e., the methoxybenzocoumarin moiety) with the side chain (i.e., the methylisobutylamide moiety) in the non-polar solvents.

To further demonstrate the sensitivity of MBC-IA to the surrounding environment, its fluorescence spectra were obtained in mixtures of aprotic and apolar 1,4-dioxane ($\alpha = 0.00, D = 2.2$) and protic and polar trifluoroethanol ($\alpha = 1.51, D = 26.8$). As shown in Fig. 4, the fluorescence intensity of MBC-IA dramatically increased as the molar ratio of trifluoroethanol in the mixture increased. These results are in accordance with the general observation that MBC-IA emits more strongly in more protic, polar media.

**Fluorescence properties of poly(NIPAM-co-MBC-AA)**

Next, poly(NIPAM-co-MBC-AA) ($m:n = 100:0.06$ in Fig. 1, $M_w = 125,000, M_n = 41,000, and M_w/M_n = 3.04$) was prepared by random copolymerization, and its fluorescence properties were investigated. First, the fluorescence spectra of poly(NIPAM-co-MBC-AA) were obtained in organic solvents (1,4-dioxane, acetonitrile, ethanol, and methanol). In these solvents, poly(NIPAM-co-MBC-AA) takes a flexible form, and the hydrodynamic diameter of poly(NIPAM-co-MBC-AA) at 20 °C were estimated by DLS measurements to be $10.35 \pm 0.36, 8.00 \pm 1.24, 15.95 \pm 0.84,$ and $10.22 \pm 1.70$ nm in 1,4-dioxane, acetonitrile, ethanol, and methanol, respectively (Fig. S2†). As shown in Fig. 5, poly(NIPAM-co-MBC-AA) emitted stronger fluorescence at longer wavelengths in a more protic, polar solvent. Thus, the sensitivity of the methoxybenzocoumarin fluorophore (i.e., MBC) to the surrounding environment was preserved, even when it was introduced into a polymer structure.

Finally, the fluorescence properties of poly(NIPAM-co-MBC-AA) in water (hydrodynamic diameter: $12.40 \pm 1.55$ nm at 20 °C, Fig. S2‡) were evaluated by changing the temperature. Fig. 6a and b show the fluorescence responses of poly(NIPAM-co-MBC-AA) to increasing temperatures. This fluorescence behavior is attributable to change in the microenvironment of the NIPAM units that occurs at approximately 32 °C: solvent water molecules are repelled from the NIPAM units at temperatures higher than 32 °C. As displayed in Fig. 6c, the fluorescence response of poly(NIPAM-co-MBC-AA) to the temperature variation was highly reproducible over ten cycles of heating and cooling, whereas that of poly(NIPAM-co-MBC-AE) lacked stability and sensitivity. The difference in the functional reproducibility between poly(NIPAM-co-MBC-AA) and poly(NIPAM-co-MBC-AE) was attributed to the robustness of the fluorescent units. Aliquots of aqueous poly(NIPAM-co-MBC-AA) and poly(NIPAM-co-MBC-AE) after ten cycles of functional assessment (heating to 45 °C and cooling to 25 °C) were analyzed by GPC with a fluorescence detector. As indicated in Fig. 6d, the MBC-AE units of poly(NIPAM-co-MBC-AA) remained unchanged during the heating and cooling cycles, whereas the MBC-AE units of poly(NIPAM-co-MBC-AE) decomposed significantly. The ester linkage of MBC-AE units was easily hydrolyzed, even in neutral aqueous solution. The fluorophore cleaved from poly(NIPAM-co-MBC-AE) was no longer sensitive to the heat-induced local environmental change near the NIPAM units, resulting in the deterioration of the function as seen in Fig. 6c. On the other hand, the new fluorescent monomer MBC-AA does not exhibit the low stability of the conventional monomer MBC-AE.

In the fluorescence response of poly(NIPAM-co-MBC-AA) in water (Fig. 6a), the maximum emission wavelength shifted from 520 to 470 nm as the temperature increased from 30 to 40 °C. This remarkable spectral shift enabled us to consider using poly(NIPAM-co-MBC-AA) as a ratiometric fluorescent thermometer. Fig. 6d shows the relationship between the fluorescence intensity ratio of poly(NIPAM-co-MBC-AA) at 470 and 520 nm ($FI_{470}/FI_{520}$) and the temperature. The $FI_{470}/FI_{520}$ value was also highly reproducible over ten cycles of heating and cooling (Fig. 6e). Although the functional temperature range was relatively narrow, the average sensitivity of the fluorescence intensity ratio ($FI_{470}/FI_{520}$) of poly(NIPAM-co-MBC-AA) as the temperature varied from 32 to 38 °C was 15.0% °C$^{-1}$, which is much higher than those of the conventional ratiometric fluorescent thermometers functioning in water, such as fluorophore(s)-labeled thermo-responsive polymers (3.4–11.3% °C$^{-1}$), which is much higher than those of the conventional ratiometric fluorescent thermometers functioning in water, such as fluorophore(s)-labeled thermo-responsive polymers (3.4–11.3% °C$^{-1}$), fluorophore(s)- and/or lumophore(s)-containing polymer nanoparticles (2.0–4.2% °C$^{-1}$), emissive inorganic nanoparticles (0.26–3.1% °C$^{-1}$), a small organic
molecule (2.7% °C\textsuperscript{−1})\textsuperscript{,24} GFP (1.3% °C\textsuperscript{−1})\textsuperscript{,25} and others (1.7–3.9% °C\textsuperscript{−1})\textsuperscript{,26} (see Table S1\textsuperscript{†} for a detailed comparison). The high sensitivity of poly(NIPAM-co-MBC-AA) clearly originated from the environment-sensitive MBC-AA units. Furthermore, poly(NIPAM-co-MBC-AA) has several advantages in ratiometric temperature sensing because (a) it requires only a single excitation to exhibit fluorescence at two different wavelengths; (b) the MBC-AA unit is pH insensitive because of the lack of a pH-sensitive structure, such as an amino group or a phenolic hydroxyl group; and (c) it contains only one fluorophore, which reduces the possibility of undesirable interactions with bio-relevant molecules when applied to probe cellular temperatures. In summary, the new fluorescent monomer MBC-AA is expected to aid in the development of novel functional polymeric sensors, especially because MBC-AA is highly robust and highly sensitive to environmental changes. In the near future, new stimulus-responsive polymeric materials will be created through the application of MBC-AA. Our research group is now pursuing this research direction.

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