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A recyclable polyoxometalate-based supramolecular chemosensor for efficient detection of carbon dioxide†

Haibing Wei,^{ab} Jinlong Zhang,^a Nan Shi,^a Yang Liu,^a Ben Zhang,^a Jie Zhang^{*a} and Xinhua Wan^{*a}

A new type of supramolecular chemosensor based on the polyoxometalate (POM) Na₉DyW₁₀O₃₆ (DyW₁₀) and the block copolymer poly(ethylene oxide-*b*-*N,N*-dimethylaminoethyl methacrylate) (PEO₁₁₄-*b*-PDMAEMA₁₆) is reported. By taking advantage of the CO₂ sensitivity of PDMAEMA blocks to protonate the neutral tertiary amino groups, CO₂ can induce the electrostatic coassembly of anionic DyW₁₀ with protonated PDMAEMA blocks, and consequently trigger the luminescence chromism of DyW₁₀ due to the change in the microenvironment of Dy³⁺. The hybrid complex in dilute aqueous solution is very sensitive to CO₂ content and shows rapid responsiveness in luminescence. The luminescence intensity of the DyW₁₀/PEO-*b*-PDMAEMA complex increases linearly with an increasing amount of dissolved CO₂, which permits the qualitative and quantitative detection of CO₂. The complex solution also shows good selectivity for CO₂, with good interference tolerance of CO, N₂, HCl, H₂O and SO₂. The supramolecular chemosensor can be recycled through disassembly of the hybrid complex by simply purging with inert gases to remove CO₂.

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Introduction

Carbon dioxide (CO₂) is a known greenhouse gas which is responsible for global climate change and also related to many human diseases, such as hypercapnia, hypocapnia and metabolic disorders, as well as being important in coalmine safety and volcanic activity.¹ CO₂ sensing and detecting is of great significance. For example, monitoring of dissolved CO₂ in arterial blood allows a timely clinical response in the case of patients with pneumonia or acute respiratory distress syndrome.² Nowadays, CO₂ detecting and sensing methods, including electrochemical systems,³ near-infrared spectroscopic techniques,⁴ gas chromatography⁵ and optical chemosensors⁶ are well-established. Among these, state-of-the-art Severinghaus-type electrochemical CO₂ sensors are widely used in commercial clinical blood gas analyzers, but these probes still suffer from a long response time and are only capable of detecting a relatively high CO₂ concentration, because their working performance relies on diffusion and the establishment

of an equilibrium between the internal pH electrode and the sample.⁷ Alternatively, CO₂ chemosensor systems based on colorimetric and fluorimetric analysis take advantage of the outcome of chromism visible to the naked eye, which can be helpful for rapid on-site monitoring.⁸ A few pH indicators or pH dependent fluorescent dyes have been used to produce such a type of optical sensor.^{6a,8c-e} However, pH-dependent organic chromatic molecules that can simultaneously meet the needs of appropriate pK_a, specificity, photostability, and contrast are very limited.

Supramolecular chemosensors are promising candidates to overcome the limitations of conventional optical chemosensors. Specially designed supramolecular chemosensors are fabricated by noncovalent binding between the molecular recognizer and the molecular reporter, and the sensing works by a relay mechanism:⁹ the recognizer detects the analyte, then communicates with the reporter by physical or chemical means, and eventually the optical signals of the reporter are switched on. This strategy integrates the complementary functions of multiple components, and is advantageous for CO₂ sensing in that it greatly expands the options of chromatic molecules and improves sensitivity and stability. In addition, by taking advantage of the dynamic nature of the noncovalent binding of supramolecular systems, device recyclability can be achieved, which is crucial for low cost and environmental concerns. Tang *et al.*^{8b} developed a CO₂ sensor based on a fluorogen with aggregation-induced emission in dipropylamine. Besides this, supramolecular CO₂ sensors are still rare and it is a challenge to

^aBeijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: jz10@pku.edu.cn; xhwan@pku.edu.cn

^bSchool of Chemistry and Chemical Engineering, Provincial Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei, Anhui 230009, China

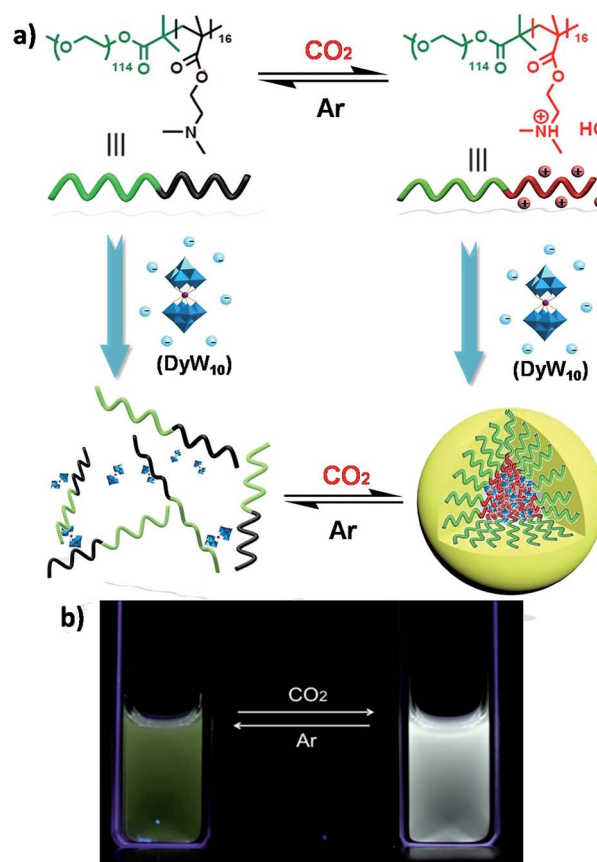
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elaborately construct a supramolecular system for CO₂ detection with the characteristics of high sensitivity, low detection limit, specificity, photostability, and recyclability.

Recently we have discovered hybrid supramolecular systems with the variable luminescence properties of lanthanide-containing polyoxometalates (POMs) by coacervate complexation with block polyelectrolytes.¹⁰ The lanthanide-containing polyoxometalates possess excellent photoluminescent properties, *i.e.* narrow emission bands, large Stokes shifts, long lifetimes and photostability, and are sensitive to ambient chemical environments.¹¹ The dysprosium-containing POM Na₉DyW₁₀O₃₆ (DyW₁₀) has two characteristic emission bands, *viz.*, ⁴F_{9/2} → ⁶H_{15/2} (blue emission, λ_{em}^{max} = 476 nm) and ⁴F_{9/2} → ⁶H_{13/2} (yellow emission, λ_{em}^{max} = 574 nm) transitions, and their relative intensity ratio $I_{4F_{9/2} \rightarrow 6H_{13/2}}/I_{4F_{9/2} \rightarrow 6H_{15/2}}$ varies according to the surrounding microenvironment, which results in luminescence chromism.^{11a,12} Although the luminescence of lanthanide-containing POMs is not sensitive to CO₂, assembly approaches can effectively tune their emission colors and intensities, and therefore their characteristics are promising when employed as supramolecular sensors.¹³ In the present work, we constructed a DyW₁₀-based supramolecular chemosensor for CO₂ detection and quantitation in aqueous systems with high sensitivity and specificity, rapid response and recyclability. Unlike previous CO₂ chemosensors, which depend primarily on chromism of organic fluorogens at the molecular level, our supramolecular CO₂ sensor is based on hybrid core-shell assemblies composed of the block copolymer poly(ethylene oxide-*b*-*N,N*-dimethylaminoethyl methacrylate) (PEO₁₁₄-*b*-PDMAEMA₁₆) and DyW₁₀ in aqueous solution. By taking advantage of the CO₂ sensitivity of PDMAEMA blocks to protonate the neutral tertiary amino groups,¹⁴ CO₂ can induce the electrostatic coassembly of anionic DyW₁₀ with protonated PDMAEMA blocks, and consequently trigger the luminescence chromism of DyW₁₀ due to the change in the microenvironment of Dy³⁺ (Scheme 1a). The luminescence variation is closely related to the CO₂ content in solution, which can be used to quantitate dissolved CO₂.

Results and discussion

The DyW₁₀/PEO-*b*-PDMAEMA complex was prepared by the addition of PEO-*b*-PDMAEMA to a dilute DyW₁₀ solution (0.2 mg mL⁻¹, 9.8 mL), where the molar ratio of tertiary amino groups in PDMAEMA to DyW₁₀ was set as 13.5 (the charge ratio of DyW₁₀/PDMAEMA ~1.0). Bubbling a small volume of CO₂ gas through the solution in as short a time as <1 minute caused a striking change in the emission of DyW₁₀ from weak green light to intense white light (Scheme 1b), while bubbling CO₂ into dilute DyW₁₀ solution for a long time did not cause a color change. The quantum yield of the DyW₁₀/PEO-*b*-PDMAEMA complex increased from 0.78% to 2.10% after treatment with CO₂, while the molar absorptivity was almost unchanged (~7.0 × 10³ L mol⁻¹ cm⁻¹ on the basis of Na₉DyW₁₀O₃₆). As a potential CO₂ sensor, the complex solution is very sensitive to dissolved CO₂ content and shows rapid responsiveness. To track the luminescence variation at low contents of dissolved CO₂, a certain amount of saturated CO₂ aqueous solution (1.45 g L⁻¹ at 100



Scheme 1 (a) Structural change of the PEO-*b*-PDMAEMA block copolymer and schematic representation of the reversible formation of a hybrid micelle after the reaction with CO₂ in aqueous medium. (b) Photos taken under illumination with 254 nm UV light, representing the CO₂-responsive luminescence chromism of the DyW₁₀/PEO-*b*-PDMAEMA complex in aqueous solution before/after CO₂ sensing.

kPa and 25 °C) was directly added to the hybrid complex solution. *In situ* PL monitoring was conducted to investigate the sensing time of the CO₂, and a substantial increase in the emission intensity was observed after only 30 s. As can be seen in Fig. 1a, the luminescence intensity of the DyW₁₀/PEO-*b*-PDMAEMA complex increased linearly with increasing content of dissolved CO₂ with a correlation coefficient of 0.9956 (Fig. 1b). As the value of $I_{4F_{9/2} \rightarrow 6H_{13/2}}/I_{4F_{9/2} \rightarrow 6H_{15/2}}$ decreased with increasing CO₂ concentration (Fig. S1†), the emission color gradually evolved from green to white, as could be seen with the naked eye. The detection limit of dissolved CO₂ was around 1.5 mg L⁻¹. The DyW₁₀/PEO-*b*-PDMAEMA sensor responds to dissolved CO₂ in the range 0–47.9 mg L⁻¹, and the linear range can be extended by changing the initial concentration of the DyW₁₀/PEO-*b*-PDMAEMA complex (Fig. S2†). Therefore, this photophysical characteristic of DyW₁₀/PEO-*b*-PDMAEMA solution allows for the qualitative and quantitative detection of CO₂. Moreover, upon exposure to air, atmospheric CO₂ (~300 ppm) can stimulate the luminescence variation of the DyW₁₀/PEO-*b*-PDMAEMA complex system (Fig. S3†), further demonstrating its high sensitivity.



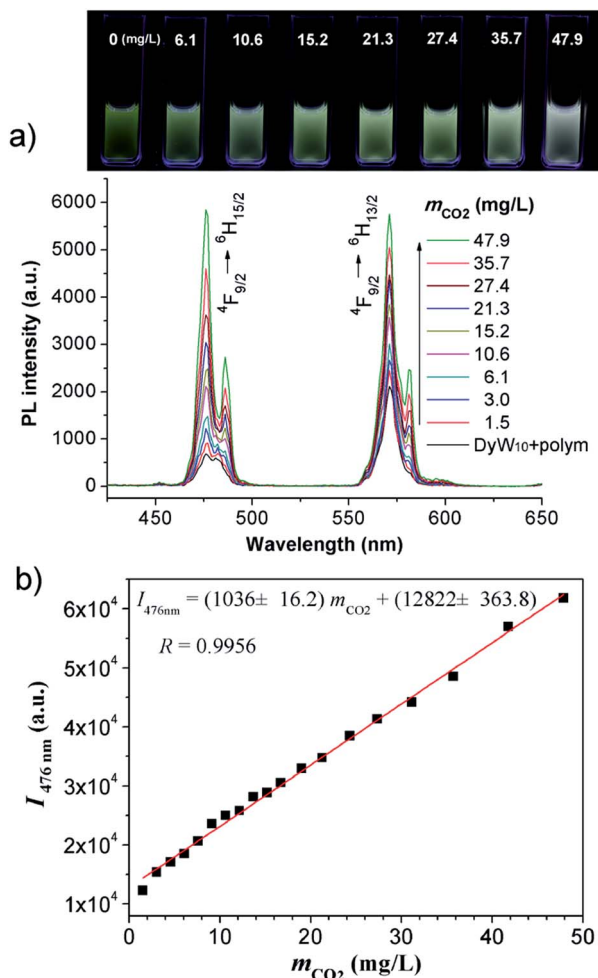


Fig. 1 (a) Variation in the PL spectra of DyW₁₀/PEO-*b*-PDMAEMA hybrid complex (DyW₁₀: 0.2 mg mL⁻¹, 9.8 mL) in the presence of various concentrations of dissolved CO₂ at 25 °C (λ_{ex} = 280 nm). Insert: photograph of DyW₁₀/PEO-*b*-PDMAEMA hybrid complex in aqueous solution with different concentrations of dissolved CO₂ under UV illumination. (b) Plot of PL integrated intensities (blue emission, $I_{476\text{nm}}$) of the DyW₁₀/PEO-*b*-PDMAEMA hybrid complex in aqueous solution as a function of dissolved CO₂ concentration at 25 °C (λ_{ex} = 280 nm).

The complex solution shows good selectivity for CO₂. CO, HCl, and SO₂ gases were purged into the solution. CO did not change the luminescence at all (Fig. S4†), while SO₂ quenched the luminescence because of the reduction of DyW₁₀ (Fig. S5†) and HCl gas also quenched the luminescence at low pH values (Fig. S6†) owing to the decomposition of DyW₁₀. However, after purging with a mixed gas containing 20% CO₂, 70% N₂, 10% O₂ and 0.1% SO₂, the complex solution still showed good detection of CO₂ (Fig. S7†), indicating that in practical applications CO, SO₂ and O₂ would not affect the CO₂ detection.

Furthermore, the sensor can be recycled by purging with inert gas to degas CO₂. As shown in Fig. 2a, the emission spectrum of the complex solution after CO₂ treatment displays two intense blue and yellow bands, with an $I_{4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}}/I_{4\text{F}_{9/2} \rightarrow 6\text{H}_{15/2}}$ value of ~ 0.92 . After purging with Ar to degas CO₂, the intensity strikingly decreased to the initial value

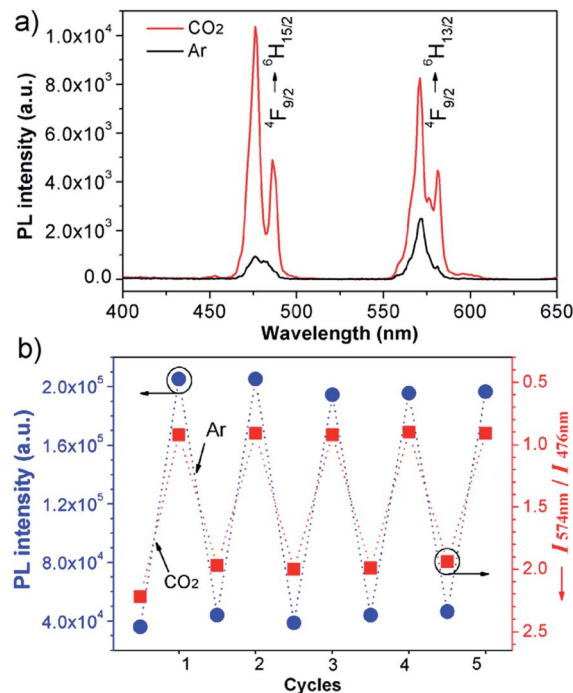


Fig. 2 (a) Emission spectra (λ_{ex} = 280 nm) of DyW₁₀/PEO-*b*-PDMAEMA coassembly in water before and after CO₂ treatment. (b) Reversible switching of the luminescence intensity and chromism of the DyW₁₀/PEO-*b*-PDMAEMA solution by alternating CO₂/Ar treatment.

before CO₂ treatment. $I_{4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}}/I_{4\text{F}_{9/2} \rightarrow 6\text{H}_{15/2}}$ also increased to ~ 2.22 , and correspondingly the emissive color recovered from strong white to the original weak green. Aside from Ar, the luminescence can be restored by purging with N₂ or simply heating, although the heating treatment takes longer (Fig. S8 and S9†). Unlike Ar and N₂, compressed air is inefficient (Fig. S10†), which may be attributed to the fact that the air contains a small amount of CO₂ (~ 300 ppm). On the other hand, the complex solution in both states is very stable in an airtight environment, with no distinct changes after standing at room temperature for at least 30 h (Fig. S11†). Both the luminescence intensity and emission color of the DyW₁₀/PEO-*b*-PDMAEMA complex can be reversibly switched by alternating CO₂/Ar treatment for at least five cycles (Fig. 2b), which endows this complex system with the merit of recyclability, making it a more affordable CO₂ detector.

To verify the CO₂-responsive assembly behavior of DyW₁₀/PEO-*b*-PDMAEMA, we used *in situ* small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and ¹H NMR spectroscopy. The scattering intensity $I(q)$ of the DyW₁₀/copolymer complex at low q values became stronger after purging CO₂ into the complex solution (Fig. 3a), supporting the formation of large assembled aggregates. The corresponding pair-distance distribution function $p(r)$ (Fig. 3b) was deduced by using Generalized Indirect Fourier Transform (GIFT) analysis,¹⁵ and the result shows that the scattering objects have a globular, almost spherical shape with an average diameter of ~ 12 nm. The TEM image of DyW₁₀/PEO-*b*-PDMAEMA assemblies after

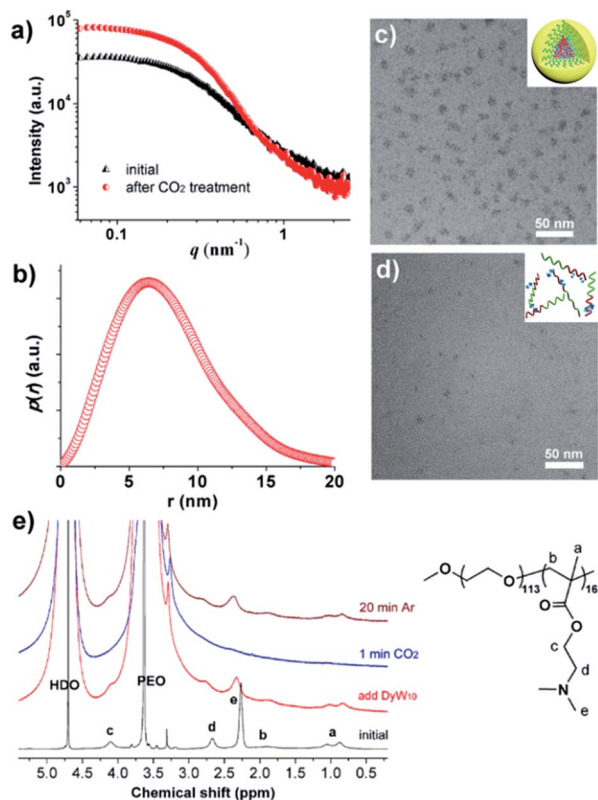


Fig. 3 Characterization of the morphology of the DyW₁₀/PEO-*b*-PDMAEMA coassemblies before and after CO₂ treatment. (a) The SAXS pattern obtained for DyW₁₀/PEO-*b*-PDMAEMA and (b) the corresponding distance distribution, $p(r)$, after treatment with CO₂; TEM images of DyW₁₀/PEO-*b*-PDMAEMA coassemblies after CO₂ (c) and Ar (d) treatment; (e) partial ¹H NMR spectra in D₂O recorded for the DyW₁₀/PEO-*b*-PDMAEMA complex, followed by purging with CO₂ gas, and then degassing CO₂ with Ar.

CO₂ treatment displays spherical micelles with an average diameter of 10 nm with a narrow distribution (Fig. 3c), in good agreement with the SAXS results, while before CO₂ treatment the TEM image displays a lesser amount of small irregular aggregates (Fig. 3d). To probe the PDMAEMA segments participating in the formation of a micellar core with the macroanionic DyW₁₀, ¹H NMR spectroscopy was utilized to characterize the signal changes of the PDMAEMA segments in D₂O solution (Fig. 3e). As expected, compared to the characteristic signals of PDMAEMA at chemical shifts ~2.38, 2.81 and 4.15 ppm recorded for the initial solution, the PDMAEMA signals disappeared completely after CO₂ treatment, indicating that almost all PDMAEMA segments participate in the formation of the coacervate core. Furthermore, the ¹H NMR signals of the PDMAEMA blocks can be restored upon treatment with Ar. All the above results support the co-assembly of DyW₁₀ and PEO-*b*-PDMAEMA after CO₂ treatment into dense spherical micelles, and the fact that the assembly/disassembly can be reversibly switched by alternating CO₂/Ar treatment.

To explore the microenvironment variations of the lumiphore DyW₁₀ before and after purging with CO₂, further examination of the decay lifetimes of DyW₁₀/PEO-*b*-PDMAEMA

coassemblies was carried out (Fig. S12†). It is known that the emission of Dy³⁺ is highly dependent on coordinated water, due to radiationless deactivation of the ⁴F_{9/2} excited state through weak coupling with the vibrational states of the high-frequency OH oscillators in the water ligands.¹⁶ In the initial state without CO₂, three lifetimes could be identified: $\tau_1 \approx 4.0 \mu\text{s}$ ($f_1 = 0.366$), $\tau_2 \approx 17.3 \mu\text{s}$ ($f_2 = 0.201$), and $\tau_3 \approx 59.9 \mu\text{s}$ ($f_3 = 0.433$) (f_i denotes the fractional contribution to the total fluorescence decay; detailed fitting methods and results are available in Table S1†).¹⁷ As the lifetime is correlated to the water molecules coordinated to the Dy³⁺ ion, the number of water ligands $q_{\text{H}_2\text{O}}$ can be estimated to be about 6.2, 1.2, and 0.16, respectively,¹⁸ demonstrating that there are a considerable number of water molecules coordinated to Dy³⁺ in the initial state (detailed calculation of $q_{\text{H}_2\text{O}}$ is given in the ESI†). In comparison, after addition of CO₂, there is only a single long decay lifetime of ~57.5 μs with a $q_{\text{H}_2\text{O}}$ value of 0.18, which is comparable to that of DyW₁₀ crystals ($\tau \approx 58.2 \mu\text{s}$, $q_{\text{H}_2\text{O}} \sim 0.17$), indicating there are almost no water molecules coordinated to the Dy³⁺ ion. This result further suggests that after CO₂ treatment DyW₁₀ is located in a relatively hydrophobic environment in the complex core of spherical micelles, where the cationic PDMAEMA segments have strong enough electrostatic affinity to the anionic DyW₁₀ to replace the water ligands.

What follows is a proposed mechanism of how CO₂ triggers the luminescence chromism. In the initial DyW₁₀/PEO-*b*-PDMAEMA dilute solution, the degree of protonation of the PDMAEMA blocks is estimated to be ~61% based on the initial pH value ~7.20 of the DyW₁₀/PEO-*b*-PDMAEMA solution (see ESI†). The water molecules coordinated to Dy³⁺ are only partially replaced by PDMAEMA segments through electrostatic interactions, which in fact lowers the D_{4d} symmetry of DyW₁₀ in the solid to C_{4v} , because the water molecules cannot lie exactly in the reflection plane of the alternating S_8 axis. The $I_{4F_{9/2} \rightarrow 6H_{13/2}}/I_{4F_{9/2} \rightarrow 6H_{15/2}}$ value ~2.22 as a probe of Dy³⁺ symmetry in ambient microenvironments also demonstrates that DyW₁₀ is located in a relatively asymmetrical microenvironment. In the presence of CO₂, the *N,N*-dimethylaminoethyl tertiary amino groups of PEO-*b*-PDMAEMA are almost completely converted to positively-charged ammonium bicarbonates (Scheme 1), and the PDMAEMA block is almost fully positively charged with $\delta \sim 99.8\%$ as estimated from the pH value ~4.80. Consequently, the electrostatic interactions between the cationic copolymer and macroanionic DyW₁₀ are greatly enhanced and drive their co-assembly into dense spherical micelles consisting of a hydrophobic PDMAEMA/DyW₁₀ complex core stabilized by a corona of neutral hydrophilic PEO blocks. As DyW₁₀ is located in the dense core of the micelles, its bound water molecules are almost completely replaced by the protonated PDMAEMA segments, and thus the symmetric microenvironment of DyW₁₀ is improved as evidenced by a decrease in the $I_{4F_{9/2} \rightarrow 6H_{13/2}}/I_{4F_{9/2} \rightarrow 6H_{15/2}}$ value to 0.92, which is comparable to that of DyW₁₀ crystals. As a result, the luminescence intensity is greatly enhanced and the chromism from green to white occurs. On purging with Ar to remove CO₂, the spherical micelles can disassemble because of the partial deprotonation of PDMAEMA, and consequently the complex solution can be used



for recyclable CO₂ sensing. Its performance does not decline with the number of cycles, because the CO₂/Ar switching does not cause any salt accumulation or contamination which would destroy the electrostatic assemblies.

Conclusions

In summary, we have demonstrated a novel supramolecular assay for fluorimetric sensing of carbon dioxide based on a POM/copolymer hybrid complex. PDMAEMA blocks could be protonated by CO₂ leading to electrostatic co-assembly with DyW₁₀, and consequently the white emission of DyW₁₀ is switched on. The fluorimetric characteristics of DyW₁₀/PEO-*b*-PDMAEMA coassemblies permit the detection of CO₂ with the merits of simplicity, sensitivity, specificity, interference tolerance, and recyclability. Furthermore, our findings may pave the way to the elaborate design of smart supramolecular materials with complementary functional components.

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