

Cite this: *Chem. Sci.*, 2015, **6**, 7201

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

Haibing Wei,<sup>ab</sup> Jinlong Zhang,<sup>a</sup> Nan Shi,<sup>a</sup> Yang Liu,<sup>a</sup> Ben Zhang,<sup>a</sup> Jie Zhang<sup>\*a</sup> and Xinhua Wan<sup>\*a</sup>

A new type of supramolecular chemosensor based on the polyoxometalate (POM)  $\text{Na}_9\text{DyW}_{10}\text{O}_{36}$  ( $\text{DyW}_{10}$ ) and the block copolymer poly(ethylene oxide-*b*-*N,N*-dimethylaminoethyl methacrylate) ( $\text{PEO}_{114-}b-\text{PDMAEMA}_{16}$ ) is reported. By taking advantage of the  $\text{CO}_2$  sensitivity of PDMAEMA blocks to protonate the neutral tertiary amino groups,  $\text{CO}_2$  can induce the electrostatic coassembly of anionic  $\text{DyW}_{10}$  with protonated PDMAEMA blocks, and consequently trigger the luminescence chromism of  $\text{DyW}_{10}$  due to the change in the microenvironment of  $\text{Dy}^{3+}$ . The hybrid complex in dilute aqueous solution is very sensitive to  $\text{CO}_2$  content and shows rapid responsiveness in luminescence. The luminescence intensity of the  $\text{DyW}_{10}/\text{PEO}-b-\text{PDMAEMA}$  complex increases linearly with an increasing amount of dissolved  $\text{CO}_2$ , which permits the qualitative and quantitative detection of  $\text{CO}_2$ . The complex solution also shows good selectivity for  $\text{CO}_2$ , with good interference tolerance of  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . The supramolecular chemosensor can be recycled through disassembly of the hybrid complex by simply purging with inert gases to remove  $\text{CO}_2$ .

Received 5th June 2015  
Accepted 3rd September 2015  
DOI: 10.1039/c5sc02020d  
[www.rsc.org/chemicalscience](http://www.rsc.org/chemicalscience)

## Introduction

Carbon dioxide ( $\text{CO}_2$ ) 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.<sup>1</sup>  $\text{CO}_2$  sensing and detecting is of great significance. For example, monitoring of dissolved  $\text{CO}_2$  in arterial blood allows a timely clinical response in the case of patients with pneumonia or acute respiratory distress syndrome.<sup>2</sup> Nowadays,  $\text{CO}_2$  detecting and sensing methods, including electrochemical systems,<sup>3</sup> near-infrared spectroscopic techniques,<sup>4</sup> gas chromatography<sup>5</sup> and optical chemosensors<sup>6</sup> are well-established. Among these, state-of-the-art Severinghaus-type electrochemical  $\text{CO}_2$  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  $\text{CO}_2$  concentration, because their working performance relies on diffusion and the establishment

of an equilibrium between the internal pH electrode and the sample.<sup>7</sup> Alternatively,  $\text{CO}_2$  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.<sup>8</sup> A few pH indicators or pH dependent fluorescent dyes have been used to produce such a type of optical sensor.<sup>6a,8c-e</sup> However, pH-dependent organic chromatic molecules that can simultaneously meet the needs of appropriate  $\text{pK}_a$ , 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:<sup>9</sup> 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  $\text{CO}_2$  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.*<sup>8b</sup> developed a  $\text{CO}_2$  sensor based on a fluorogen with aggregation-induced emission in dipropylamine. Besides this, supramolecular  $\text{CO}_2$  sensors are still rare and it is a challenge to

<sup>a</sup>Beijing 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](mailto:jz10@pku.edu.cn); [xhwan@pku.edu.cn](mailto:xhwan@pku.edu.cn)

<sup>b</sup>School of Chemistry and Chemical Engineering, Provincial Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei, Anhui 230009, China

† Electronic supplementary information (ESI) available. See DOI: [10.1039/c5sc02020d](https://doi.org/10.1039/c5sc02020d)

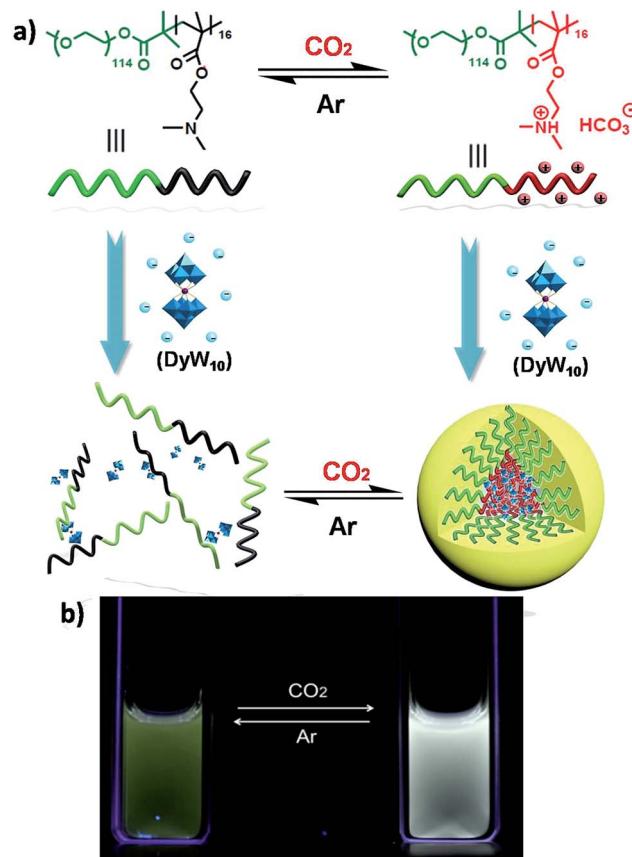


elaborately construct a supramolecular system for  $\text{CO}_2$  detection with the characteristics of high sensitivity, low detection limit, specificity, photostability, and recyclability.

Recently we have discovered hybrid supramolecular systems with the variable luminescence properties of lanthanide-containing polyoxometalates (POMs) by coacervate complexation with block polyelectrolytes.<sup>10</sup> 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.<sup>11</sup> The dysprosium-containing POM  $\text{Na}_9\text{DyW}_{10}\text{O}_{36}$  ( $\text{DyW}_{10}$ ) has two characteristic emission bands, *viz.*,  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$  (blue emission,  $\lambda_{\text{em}}^{\text{max}} = 476 \text{ nm}$ ) and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  (yellow emission,  $\lambda_{\text{em}}^{\text{max}} = 574 \text{ nm}$ ) transitions, and their relative intensity ratio  $I_{\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}}/I_{\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}}$  varies according to the surrounding microenvironment, which results in luminescence chromism.<sup>11a,12</sup> Although the luminescence of lanthanide-containing POMs is not sensitive to  $\text{CO}_2$ , assembly approaches can effectively tune their emission colors and intensities, and therefore their characteristics are promising when employed as supramolecular sensors.<sup>13</sup> In the present work, we constructed a  $\text{DyW}_{10}$ -based supramolecular chemosensor for  $\text{CO}_2$  detection and quantitation in aqueous systems with high sensitivity and specificity, rapid response and recyclability. Unlike previous  $\text{CO}_2$  chemosensors, which depend primarily on chromism of organic fluorogens at the molecular level, our supramolecular  $\text{CO}_2$  sensor is based on hybrid core–shell assemblies composed of the block copolymer poly(ethylene oxide-*b*-*N,N*-dimethylaminoethyl methacrylate) ( $\text{PEO}_{114}\text{-}b\text{-PDMAEMA}_{16}$ ) and  $\text{DyW}_{10}$  in aqueous solution. By taking advantage of the  $\text{CO}_2$  sensitivity of PDMAEMA blocks to protonate the neutral tertiary amino groups,<sup>14</sup>  $\text{CO}_2$  can induce the electrostatic coassembly of anionic  $\text{DyW}_{10}$  with protonated PDMAEMA blocks, and consequently trigger the luminescence chromism of  $\text{DyW}_{10}$  due to the change in the microenvironment of  $\text{Dy}^{3+}$  (Scheme 1a). The luminescence variation is closely related to the  $\text{CO}_2$  content in solution, which can be used to quantitate dissolved  $\text{CO}_2$ .

## Results and discussion

The  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex was prepared by the addition of  $\text{PEO-}b\text{-PDMAEMA}$  to a dilute  $\text{DyW}_{10}$  solution ( $0.2 \text{ mg mL}^{-1}$ ,  $9.8 \text{ mL}$ ), where the molar ratio of tertiary amino groups in PDMAEMA to  $\text{DyW}_{10}$  was set as 13.5 (the charge ratio of  $\text{DyW}_{10}/\text{PDMAEMA} \sim 1.0$ ). Bubbling a small volume of  $\text{CO}_2$  gas through the solution in as short a time as  $<1$  minute caused a striking change in the emission of  $\text{DyW}_{10}$  from weak green light to intense white light (Scheme 1b), while bubbling  $\text{CO}_2$  into dilute  $\text{DyW}_{10}$  solution for a long time did not cause a color change. The quantum yield of the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex increased from 0.78% to 2.10% after treatment with  $\text{CO}_2$ , while the molar absorptivity was almost unchanged ( $\sim 7.0 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  on the basis of  $\text{Na}_9\text{DyW}_{10}\text{O}_{36}$ ). As a potential  $\text{CO}_2$  sensor, the complex solution is very sensitive to dissolved  $\text{CO}_2$  content and shows rapid responsiveness. To track the luminescence variation at low contents of dissolved  $\text{CO}_2$ , a certain amount of saturated  $\text{CO}_2$  aqueous solution ( $1.45 \text{ g L}^{-1}$  at 100



**Scheme 1** (a) Structural change of the  $\text{PEO-}b\text{-PDMAEMA}$  block copolymer and schematic representation of the reversible formation of a hybrid micelle after the reaction with  $\text{CO}_2$  in aqueous medium. (b) Photos taken under illumination with 254 nm UV light, representing the  $\text{CO}_2$ -responsive luminescence chromism of the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex in aqueous solution before/after  $\text{CO}_2$  sensing.

kPa and  $25^\circ\text{C}$ ) was directly added to the hybrid complex solution. *In situ* PL monitoring was conducted to investigate the sensing time of the  $\text{CO}_2$ , 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  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex increased linearly with increasing content of dissolved  $\text{CO}_2$  with a correlation coefficient of 0.9956 (Fig. 1b). As the value of  $I_{\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}}/I_{\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}}$  decreased with increasing  $\text{CO}_2$  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  $\text{CO}_2$  was around  $1.5 \text{ mg L}^{-1}$ . The  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  sensor responds to dissolved  $\text{CO}_2$  in the range  $0\text{--}47.9 \text{ mg L}^{-1}$ , and the linear range can be extended by changing the initial concentration of the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex (Fig. S2†). Therefore, this photophysical characteristic of  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  solution allows for the qualitative and quantitative detection of  $\text{CO}_2$ . Moreover, upon exposure to air, atmospheric  $\text{CO}_2$  ( $\sim 300 \text{ ppm}$ ) can stimulate the luminescence variation of the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex system (Fig. S3†), further demonstrating its high sensitivity.

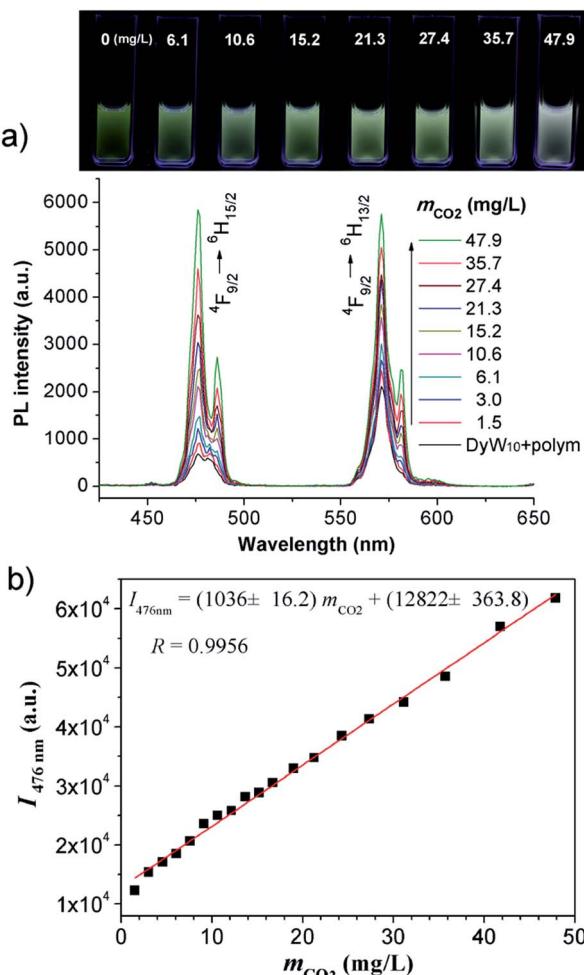


Fig. 1 (a) Variation in the PL spectra of DyW<sub>10</sub>/PEO-*b*-PDMAEMA hybrid complex (DyW<sub>10</sub>: 0.2 mg mL<sup>-1</sup>, 9.8 mL) in the presence of various concentrations of dissolved CO<sub>2</sub> at 25 °C ( $\lambda_{\text{ex}} = 280$  nm). Insert: photograph of DyW<sub>10</sub>/PEO-*b*-PDMAEMA hybrid complex in aqueous solution with different concentrations of dissolved CO<sub>2</sub> under UV illumination. (b) Plot of PL integrated intensities (blue emission,  $I_{\text{F}_{9/2} \rightarrow \text{H}_{13/2}}$ ) of the DyW<sub>10</sub>/PEO-*b*-PDMAEMA hybrid complex in aqueous solution as a function of dissolved CO<sub>2</sub> concentration at 25 °C ( $\lambda_{\text{ex}} = 280$  nm).

The complex solution shows good selectivity for CO<sub>2</sub>. CO, HCl, and SO<sub>2</sub> gases were purged into the solution. CO did not change the luminescence at all (Fig. S4†), while SO<sub>2</sub> quenched the luminescence because of the reduction of DyW<sub>10</sub> (Fig. S5†) and HCl gas also quenched the luminescence at low pH values (Fig. S6†) owing to the decomposition of DyW<sub>10</sub>. However, after purging with a mixed gas containing 20% CO<sub>2</sub>, 70% N<sub>2</sub>, 10% O<sub>2</sub> and 0.1% SO<sub>2</sub>, the complex solution still showed good detection of CO<sub>2</sub> (Fig. S7†), indicating that in practical applications CO, SO<sub>2</sub> and O<sub>2</sub> would not affect the CO<sub>2</sub> detection.

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

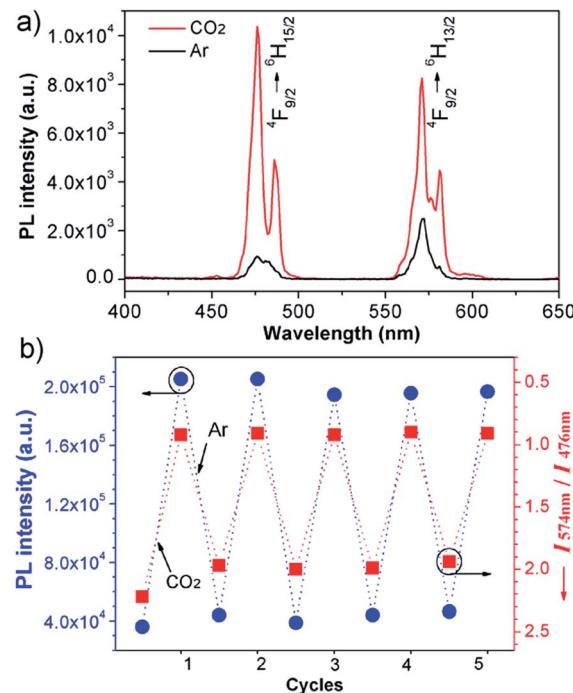


Fig. 2 (a) Emission spectra ( $\lambda_{\text{ex}} = 280$  nm) of DyW<sub>10</sub>/PEO-*b*-PDMAEMA coassembly in water before and after CO<sub>2</sub> treatment. (b) Reversible switching of the luminescence intensity and chromism of the DyW<sub>10</sub>/PEO-*b*-PDMAEMA solution by alternating CO<sub>2</sub>/Ar treatment.

before CO<sub>2</sub> treatment.  $I_{\text{F}_{9/2} \rightarrow \text{H}_{13/2}}/I_{\text{F}_{9/2} \rightarrow \text{H}_{15/2}}$  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 N<sub>2</sub> or simply heating, although the heating treatment takes longer (Fig. S8 and S9†). Unlike Ar and N<sub>2</sub>, compressed air is inefficient (Fig. S10†), which may be attributed to the fact that the air contains a small amount of CO<sub>2</sub> (~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 DyW<sub>10</sub>/PEO-*b*-PDMAEMA complex can be reversibly switched by alternating CO<sub>2</sub>/Ar treatment for at least five cycles (Fig. 2b), which endows this complex system with the merit of recyclability, making it a more affordable CO<sub>2</sub> detector.

To verify the CO<sub>2</sub>-responsive assembly behavior of DyW<sub>10</sub>/PEO-*b*-PDMAEMA, we used *in situ* small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and <sup>1</sup>H NMR spectroscopy. The scattering intensity  $I(q)$  of the DyW<sub>10</sub>/copolymer complex at low  $q$  values became stronger after purging CO<sub>2</sub> 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,<sup>15</sup> 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 DyW<sub>10</sub>/PEO-*b*-PDMAEMA assemblies after



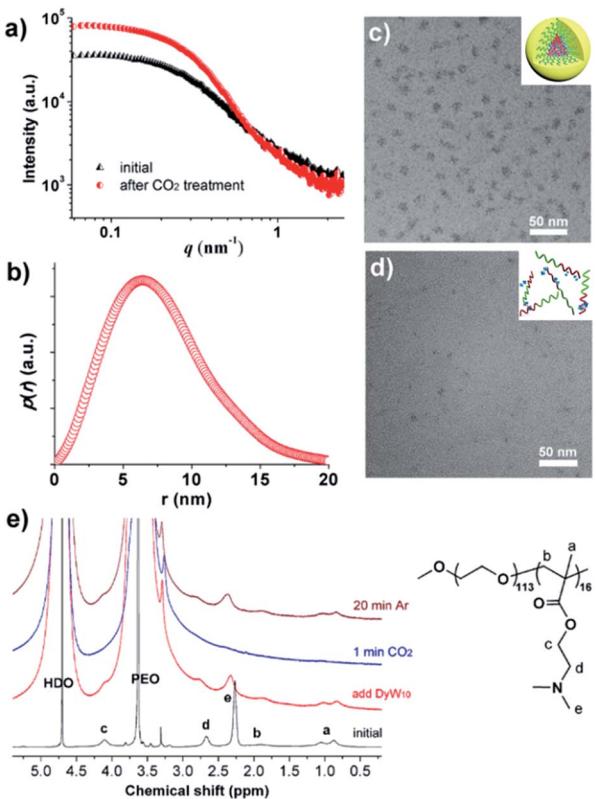


Fig. 3 Characterization of the morphology of the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  coassemblies before and after  $\text{CO}_2$  treatment. (a) The SAXS pattern obtained for  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  and (b) the corresponding distance distribution,  $p(r)$ , after treatment with  $\text{CO}_2$ ; TEM images of  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  coassemblies after  $\text{CO}_2$  (c) and Ar (d) treatment; (e) partial  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$  recorded for the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  complex, followed by purging with  $\text{CO}_2$  gas, and then degassing  $\text{CO}_2$  with Ar.

$\text{CO}_2$  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  $\text{CO}_2$  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  $\text{DyW}_{10}$ ,  $^1\text{H}$  NMR spectroscopy was utilized to characterize the signal changes of the PDMAEMA segments in  $\text{D}_2\text{O}$  solution (Fig. 3e). As expected, compared to the characteristic signals of PDMAEMA at chemical shifts  $\sim 2.38$ ,  $2.81$  and  $4.15$  ppm recorded for the initial solution, the PDMAEMA signals disappeared completely after  $\text{CO}_2$  treatment, indicating that almost all PDMAEMA segments participate in the formation of the coacervate core. Furthermore, the  $^1\text{H}$  NMR signals of the PDMAEMA blocks can be restored upon treatment with Ar. All the above results support the co-assembly of  $\text{DyW}_{10}$  and  $\text{PEO-}b\text{-PDMAEMA}$  after  $\text{CO}_2$  treatment into dense spherical micelles, and the fact that the assembly/disassembly can be reversibly switched by alternating  $\text{CO}_2$ /Ar treatment.

To explore the microenvironment variations of the lumino-phore  $\text{DyW}_{10}$  before and after purging with  $\text{CO}_2$ , further examination of the decay lifetimes of  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$

coassemblies was carried out (Fig. S12†). It is known that the emission of  $\text{Dy}^{3+}$  is highly dependent on coordinated water, due to radiationless deactivation of the  $^4\text{F}_{9/2}$  excited state through weak coupling with the vibrational states of the high-frequency OH oscillators in the water ligands.<sup>16</sup> In the initial state without  $\text{CO}_2$ , 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†).<sup>17</sup> As the lifetime is correlated to the water molecules coordinated to the  $\text{Dy}^{3+}$  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,<sup>18</sup> demonstrating that there are a considerable number of water molecules coordinated to  $\text{Dy}^{3+}$  in the initial state (detailed calculation of  $q_{\text{H}_2\text{O}}$  is given in the ESI†). In comparison, after addition of  $\text{CO}_2$ , there is only a single long decay lifetime of  $\sim 57.5 \mu\text{s}$  with a  $q_{\text{H}_2\text{O}}$  value of 0.18, which is comparable to that of  $\text{DyW}_{10}$  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  $\text{Dy}^{3+}$  ion. This result further suggests that after  $\text{CO}_2$  treatment  $\text{DyW}_{10}$  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  $\text{DyW}_{10}$  to replace the water ligands.

What follows is a proposed mechanism of how  $\text{CO}_2$  triggers the luminescence chromism. In the initial  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  dilute solution, the degree of protonation of the PDMAEMA blocks is estimated to be  $\sim 61\%$  based on the initial pH value  $\sim 7.20$  of the  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  solution (see ESI†). The water molecules coordinated to  $\text{Dy}^{3+}$  are only partially replaced by PDMAEMA segments through electrostatic interactions, which in fact lowers the  $D_{4d}$  symmetry of  $\text{DyW}_{10}$  in the solid to  $C_{4v}$ , because the water molecules cannot lie exactly in the reflection plane of the alternating  $S_8$  axis. The  $I_{^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}}/I_{^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}}$  value  $\sim 2.22$  as a probe of  $\text{Dy}^{3+}$  symmetry in ambient microenvironments also demonstrates that  $\text{DyW}_{10}$  is located in a relatively asymmetrical microenvironment. In the presence of  $\text{CO}_2$ , the *N,N*-dimethylaminoethyl tertiary amino groups of  $\text{PEO-}b\text{-PDMAEMA}$  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  $\sim 4.80$ . Consequently, the electrostatic interactions between the cationic copolymer and macroanionic  $\text{DyW}_{10}$  are greatly enhanced and drive their co-assembly into dense spherical micelles consisting of a hydrophobic PDMAEMA/ $\text{DyW}_{10}$  complex core stabilized by a corona of neutral hydrophilic PEO blocks. As  $\text{DyW}_{10}$  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  $\text{DyW}_{10}$  is improved as evidenced by a decrease in the  $I_{^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}}/I_{^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}}$  value to 0.92, which is comparable to that of  $\text{DyW}_{10}$  crystals. As a result, the luminescence intensity is greatly enhanced and the chromism from green to white occurs. On purging with Ar to remove  $\text{CO}_2$ , the spherical micelles can disassemble because of the partial deprotonation of PDMAEMA, and consequently the complex solution can be used



for recyclable  $\text{CO}_2$  sensing. Its performance does not decline with the number of cycles, because the  $\text{CO}_2/\text{Ar}$  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  $\text{CO}_2$  leading to electrostatic co-assembly with  $\text{DyW}_{10}$ , and consequently the white emission of  $\text{DyW}_{10}$  is switched on. The fluorimetric characteristics of  $\text{DyW}_{10}/\text{PEO-}b\text{-PDMAEMA}$  coassemblies permit the detection of  $\text{CO}_2$  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.

## Acknowledgements

We would like to thank Prof. Jinying Yuan at Tsinghua University for helpful discussions. This work was supported by the National Natural Science Foundation of China (21322404; 51373001; 21404030), and the Natural Science Foundation of Beijing Municipality (No. 2122024).

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