

Multi-dimensional, light-controlled switch of fluorescence resonance energy transfer based on orderly assembly of 0D dye@micro-micelles and 2D ultrathin-layered nanosheets

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ABSTRACT

Fluorescence resonance energy transfer (FRET) systems have broad applications in visual detection, intelligent materials, and biological imaging, all of which favor the transmission of light through multiple dimensions and in diverse directions. Herein, we have demonstrated multi-dimensional (0D and 2D) FRET within a multi-layer ultrathin film (UTF) by employing a layer-by-layer (LBL) assembly technique. The anionic block copolymer micelle poly(tert-butyl acrylate-co-ethyl acrylate-co-methacrylic acid) (PTBEM) is chosen as a molecular carrier for the incorporation of bis(8-hydroxyquinolate) zinc (Znq_2) and open-ring merocyanine (MC) (denoted as $(\text{Znq}_2/\text{MC})@\text{PTBEM}$). Alternatively, electrostatic assembly is performed with cationic layered double hydroxide (LDH) nanosheets (denoted as $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_n$). This $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_n$ system offers a multi-dimensional propagation medium and ensures that the FRET donor and acceptor are located within their Förster radii in each direction. The system demonstrates a FRET process that can be switched via alternating ultraviolet/visible (UV/vis) irradiation, with tunable blue–green/red fluorescence, resulting in a FRET efficiency as high as 81.7%. It is expected that this assembly method, which uses 0D micelles on a 2D layered material, can be extended to other systems for further development of multi-dimensional FRET.

1 Introduction

The conversion of nature's energy resources (such as solar, wind, and water energy) usually employs efficient

energy transfer processes, which operate through multiple dimensions and in various directions. Such fashions have enriched the mode of energy transduction and improved the efficiency of energy utilization. In

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this sense, fluorescence resonance energy transfer (FRET), which involves the transfer of light energy between a donor and an acceptor, has received much attention during last few years. This is because FRET systems are applicable to a wide range of applications such as electronic displays and biochemical imaging [1, 2]. Recently, a variety of FRET processes have been reported within nanoparticles [3–5], dendrimers [6, 7], zeolites [8], and polymer micelle films [9, 10]. Meanwhile, FRET signals can be further induced by thermal-[11], photo-[12, 13], and vapor-[14] stimuli, which have drawn increasing attention for their utility in sensors and optical memory devices [15]. However, multi-dimensional FRET is still difficult to demonstrate, because the common systems fabricated via decoration and linking of donor/acceptor components in liquid cannot provide a multi-dimensional propagation medium. Another significant obstacle is that high-efficiency FRET materials should ensure that donors and acceptors are located within their Förster radii in each direction [16, 17]. Therefore, it is essential to develop novel systems and approaches for the transmission of FRET signals in multiple dimensions and directions.

Recently, micro-micellar structures formed by amphiphilic block copolymers in aqueous media have been used to construct zero-dimensional (0D) FRET systems. For example, the micelles can incorporate two different hydrophobic fluorescent dyes simultaneously, which form an energy transfer system with individual dye molecules as the energy donors and acceptors [18, 19]. In this context, fluorescence modulation of the chromophore molecules can be achieved through a 0D intra-micelle FRET process. To develop multiple dimensional FRET systems with varied directions for photofunctional applications, we have put forth a strategy to assemble 0D micelles onto two-dimensional (2D) inorganic nanosheets and produce 0D and 2D FRET simultaneously. Layered double hydroxides (LDHs) are one type of 2D inorganic material, whose structure can be expressed by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2] (A^{n-})_{x/n} \cdot mH_2O$ (M^{II} and M^{III} are divalent and trivalent metal ions respectively, and A^{n-} is an anion) [20–23]. The exfoliated LDH nanosheets can serve as 2D building blocks for construction of ultrathin films (UTFs) with enhanced photofunc-

tionalities, and the interlayer spaces in UTFs offer a nano-sized medium for 2D interlayer energy transfer [24–26].

In this work, an anionic and amphiphilic block copolymer (poly(*tert*-butyl acrylate-co-ethyl acrylate-co-methacrylic acid), PTBEM) was chosen to incorporate two hydrophobic fluorescent dyes: bis(8-hydroxyquinolate) zinc (Znq_2 , as the donor) and open-ring merocyanine (MC, as the acceptor). Subsequently, a 2D orderly $[(Znq_2/MC)@PTBEM\ DH]_n$ UTF was fabricated via the assembly of anionic $(Znq_2/MC)@PTBEM$ micro-micelles and positively charged, exfoliated LDH nanosheets. This UTF can simultaneously realize intra-micelle 0D FRET and interlayer 2D FRET across the LDH nanosheets. Such a multi-dimensional UTF presents a much higher FRET efficiency than a single dimensional system; the fluorescence lifetime and quantum yield of the receptor (MC) are enhanced significantly. In addition, the reversible FRET process (blue–green and red fluorescence states) can be further modulated using alternating ultraviolet/visible (UV/vis) light irradiation. To the best of our knowledge, no light-controlled FRET system with both 0D and 2D FRET has been reported prior to this work. Such a multi-layered, ultrathin film exhibits properties that are promising for the development of a FRET system by immobilizing the donor and acceptor on both sides of an exfoliated nanosheet. Multi-dimensional FRET, whose FRET efficiency is normally higher than a single-dimensional system due to a synergistic effect between 0D and 2D in transmission, would serve as an improved system for energy transfer with potential applications in biochemical imaging, detection, and molecular switching [27–32].

2 Experimental

2.1 Materials

Analytical grade $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, methanamide, urea, and ethylene glycol monobutyl ether ($CH_3(CH_2)_3OCH_2CH_2OH$) were purchased from Beijing Chemical Co., Ltd. All other chemicals were analytical grade and used as received without further purification. Deionized water was

used throughout the experiments. Poly(tert-butyl acrylate-co-ethyl acrylate-co-methacrylic acid) $[\text{CH}_2\text{CH}[\text{CO}_2\text{C}(\text{CH}_3)_3]_x[\text{CH}_2\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)]_y[\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{H})]_z}$ (PTBEM) and poly(dimethyldiallylammonium chloride) (PDDA, Mw 100,000–200,000) were purchased from Sigma-Aldrich Development Co., Ltd. Poly(styrene sulfonic acid) (PSS, Mw 70,000) was purchased from J&K Chemical. Co., Ltd. 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran (spiropyran, Mw 322.36) was purchased from Tokyo Chemical Industry. Bis(8-hydroxyquinolate)-zinc ($\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2\text{Zn}$, Znq_2) was purchased from Aladdin Reagent.

2.2 Preparation of MC@PTBEM, Znq_2 @PTBEM, and (Znq_2/MC) @PTBEM micelles

The micelles were synthesized via a liquid synthesis. MC ($0.1 \text{ mg}\cdot\text{mL}^{-1}$) and Znq_2 ($0.4 \text{ mg}\cdot\text{mL}^{-1}$) were dissolved in ethylene glycol monobutyl ether (GME) to produce a solution. Then, 2 mL of MC (or Znq_2) in GME solution was added dropwise to 38 mL of a PTBEM micelle solution ($0.368 \text{ mg}\cdot\text{mL}^{-1}$, pH 7.0, adjusted using a 0.1 M NaOH solution) with intense ultrasonic treatment and stirring for 24 h. The pH values of the final MC@PTBEM and Znq_2 @PTBEM micelles were maintained at 7.0. MC and Znq_2 were mixed into GME, and 2 mL of the mixed liquor was added dropwise into 38 mL of PTBEM micelle solution with intense ultrasonic treatment and stirring for 24 h to form (Znq_2/MC) @PTBEM micelles. The resulting solution of micelles was passed through a 200 nm filter.

2.3 Preparation of the UTFs via LBL

The process for synthesis and exfoliation of MgAl-LDH nanosheets was similar to the procedure described in our previous work [33–36]. The quartz substrates were first cleaned in concentrated $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (30%) (7:3, v/v) for 30 min and then washed with pure water. The clean substrates were dipped into a PDDA solution ($1.0 \text{ g}\cdot\text{L}^{-1}$) for 20 min, then thoroughly rinsed with water and dried in air so as to obtain a positively charged surface. The pretreated substrate was immersed into the negatively charged micelles for 10 min, then washed and treated with a colloidal suspension ($1 \text{ g}\cdot\text{L}^{-1}$) of LDH nanosheets for another 10 min, before being washed thoroughly again. The multilayered

(Znq_2/MC) @PTBEM/LDH/MC@PTBEM $)_n$ UTFs were obtained via alternate deposition of Znq_2 @PTBEM micelles, exfoliated LDH nanosheets and MC@PTBEM micelles for n cycles. The multilayer $[(\text{Znq}_2/\text{MC})$ @PTBEM/LDH $)]_n$ UTFs were fabricated via alternate deposition of (Znq_2/MC) @PTBEM micelles and exfoliated LDH nanosheets for n cycles.

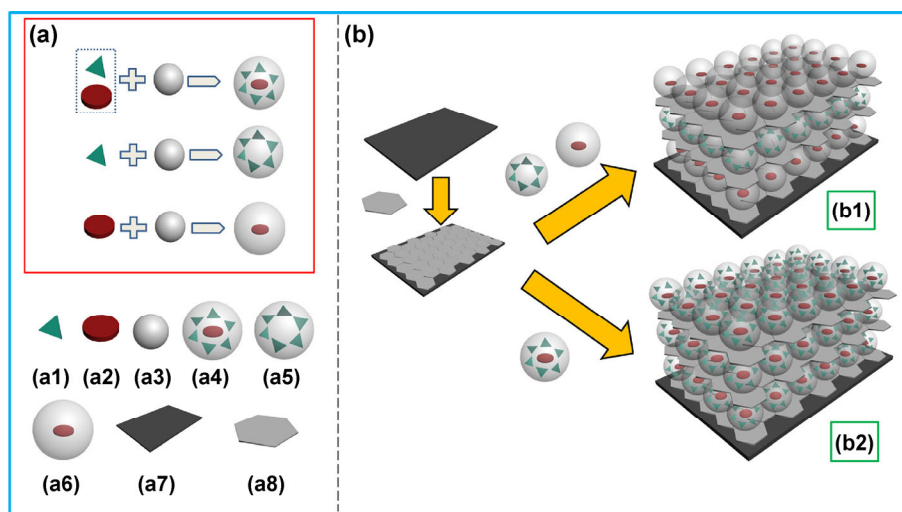
2.4 Sample characterization

Fluorescence spectra were measured on a RF-5301PC fluorospectrophotometer under identical conditions with an excitation wavelength of 365 nm. A Zeiss Supra 55 scanning electron microscope (20 kV acceleration voltage) was used to investigate the surface morphologies of the UTFs. The interlayer spacings of the films were measured using X-ray diffraction patterns (XRD) from a Rigaku 2500 VB2 + PC diffractometer under the following conditions: 40 kV, 50 mA, and Cu $K\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$). UV/vis absorption spectra were collected in the range of 320–800 nm on a Shimadzu U-3000 spectrophotometer with a slit width of 1.0 nm. The percentage contribution of each lifetime component to the total decay curve was calculated using the Edinburgh F980 instrument software.

3 Results and discussion

Spiropyran (SP) undergoes a structural transformation from closed-ring SP to an open-ring MC state via exposure to UV, and reverts back to the SP state via visible light exposure (Scheme S1 in the Electronic Supplementary Material (ESM)) [37, 38]. This switching behavior between optically transparent SP and absorptive MC produces the possibility of reversible, light-controlled changes in fluorescence [39–41]. Znq_2 (Fig. S1 in the ESM), as a metal 8-hydroxyquinolate chelate, emits at $\sim 475 \text{ nm}$ in the PTBEM micelles (Fig. S2 in the ESM). This emission matches well with the absorption of MC (Fig. S3 in the ESM). This is beneficial for effective energy transfer from Znq_2 to MC. Therefore, Znq_2 and MC can serve as ideal donors and acceptors, respectively, for the construction of a FRET system.

Scheme 1 shows the detailed synthesis process used with multi-dimensional FRET systems: (i) Znq_2 and MC are encapsulated within the same micro-micelle



Scheme 1 A schematic representation of the fabrication of multi-layer UTFs via the LBL self-assembly method: (a1) Znq_2 , (a2) MC, (a3) PTBEM, (a4) $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelles, (a5) $\text{Znq}_2@\text{PTBEM}$, (a6) $\text{MC}@\text{PTBEM}$, (a7) quartz glass substrate, (a8) LDH nanosheet; (b1) $(\text{Znq}_2@\text{PTBEM}/\text{LDH}/\text{MC}@\text{PTBEM})_n$, (b2) $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_n$.

(denoted as $(\text{Znq}_2/\text{MC})@\text{PTBEM}$) as the 0D FRET system; they are also packed into independent micelles denoted as $\text{Znq}_2@\text{PTBEM}$ and $\text{MC}@\text{PTBEM}$, respectively (Scheme 1(a)); (ii) a multi-level UTF is prepared via the LBL self-assembly of negatively charged $\text{Znq}_2@\text{PTBEM}$ and $\text{MC}@\text{PTBEM}$ micelles with positively charged LDH nanosheets (denoted as $(\text{Znq}_2@\text{PTBEM}/\text{LDH}/\text{MC}@\text{PTBEM})_n$ UTF; n represents number of cycles) as the 2D FRET system; the assembly of $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelles with LDH nanosheets results in generation of the $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_n$ UTF as a multi-dimensional FRET system (Scheme 1(b)).

3.1 Fabrication of the $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelle as a 0D FRET system

For $(\text{Znq}_2/\text{MC})@\text{PTBEM}$, the FRET donor–acceptor (Znq_2 –MC) pair is packed at a close distance in the same micelle. The micelle cannot generate FRET in visible light since SP is in a ring-closed state and the FRET process is inhibited. After irradiation with UV light, ring-closed SP transforms into ring-open MC. Subsequently, the blue–green fluorescence of Znq_2 (donor) can be transferred to MC (acceptor) via an emission at ~ 600 nm (Fig. 1(a)).

Figure 1(b) shows the modulation of fluorescence by a Znq_2 –MC pair in the micelle system. The spectrum of $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ is much different from those of dyes in GME (Fig. S4 in the ESM), which indicates

that the dye molecule is encapsulated within the PTBEM micro-micelles [42]. When the micelles are irradiated with UV light, the characteristic fluorescence emission for Znq_2 at 475 nm decreases significantly, and the emission at 600 nm increases dramatically, suggesting the occurrence of FRET from Znq_2 to MC. Upon subsequent irradiation with visible light, the fluorescence intensity at 475 nm recovers. Therefore, the FRET channel of the $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ system can be switched on and off reversibly via alternating irradiation with UV and visible light. Figure 1(c) clearly shows changes in the UV/vis spectra for this photochromic fluorescence system.

The process of energy transfer between a donor and an acceptor encapsulated in the same micelle is further analyzed via time-resolved fluorescence (TRF) of Znq_2 (donor) at 475 nm in the absence and presence of MC (acceptor) (Fig. 1(d)). The TRF of Znq_2 without any acceptor (blue line) shows a double-exponential decay with an average lifetime of 23 ns. However, when MC is encapsulated with Znq_2 in the same PTBEM micelle, the fluorescence decay of Znq_2 (red line) becomes faster, with an average lifetime of 7.1 ns. A new decay time of $\tau_3 = 1.6$ ns (54%) appears, which can be attributed to quenching of the excited Znq_2 by FRET (Table S1 in the ESM). Subsequently, the FRET efficiency (E) is measured experimentally using $E = 1 - F_{\text{DA}}/F_{\text{D}}$, where F_{DA} is the integrated fluorescence intensity

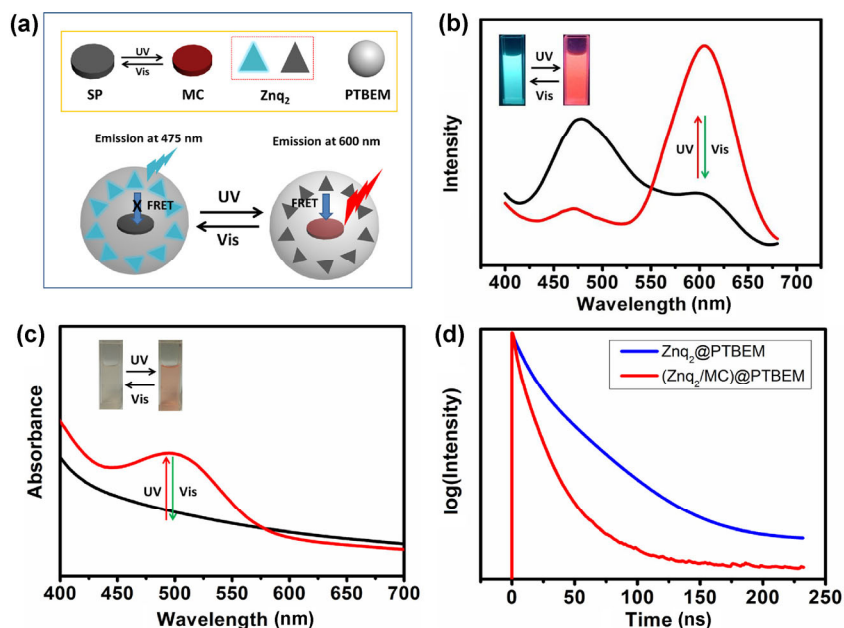


Figure 1 (a) Formation of an intra-micelle 0D FRET and reversible fluorescence modulation system by packing Znq₂ and SP into the same PTBEM micelle. (b) Reversible fluorescent transformation and (c) UV/vis absorption spectra of (Znq₂/MC)@PTBEM triggered by UV and visible light. (d) Normalized TRFs of Znq₂ alone (blue) and a Znq₂-MC mixture (red) in the same micelle at 475 nm.

of the donor in the presence of the acceptor and F_D is the integrated fluorescence intensity of the donor alone [43, 44]. The 0D FRET system can achieve an impressive efficiency of 75.24%, which is comparable to previously reported work (Table S2 in the ESM) [45].

The surface morphology of the (Znq₂/MC)@PTBEM micelles was investigated via SEM. The spheres are inerratic and orderly with diameters of 9–12 nm, which let them act as 0D confinement spaces for Znq₂ and MC (Fig. 2(a)). A further theoretical calculation shows that the average donor to acceptor distances are approximately 2.35 nm in the horizontal direction

and 0.86 nm in the vertical direction (Fig. 2(b)). This evidence demonstrates that the (Znq₂/MC)@PTBEM system exhibits an intra-micelle 0D FRET process with the aid of PTBEM micelles.

3.2 Fabrication of a (Znq₂@PTBEM/LDH/MC@PTBEM)_n UTF as 2D FRET system

To demonstrate the 2D FRET system, Znq₂ and MC are independently encapsulated within PTBEM micelles, and it is observed that the FRET cannot take place between Znq₂@PTBEM and MC@PTBEM in solution (Fig. S5 and Table S3 in the ESM). Since the gap and

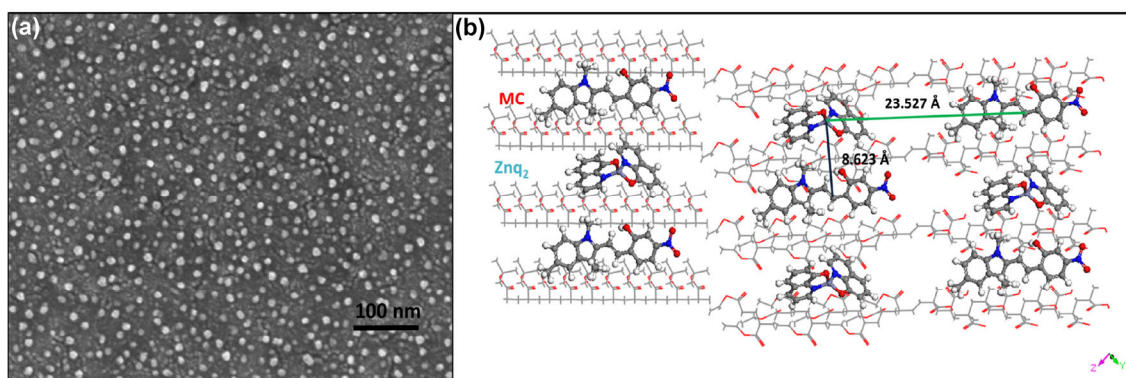


Figure 2 (a) Top-down SEM of (Znq₂/MC)@PTBEM micelles and (b) the idealized permutation distribution schematic of Znq₂ and MC isolated in PTBEM micelle.

mutual repulsion between the negative cores prohibit FRET, the phenomenon hardly takes place. After alternative assembly of $\text{Znq}_2\text{@PTBEM}$ and MC@PTBEM with LDH nanosheets (Fig. 3(a)), the negative cores of the donor and acceptor are linked closely with both sides of the positive LDH, and the shortest distance between the donor and acceptor is close to the thickness of the exfoliated LDH nanosheets (about 0.5 nm) [20, 46–48]. Based on the typical Förster FRET distance, this is acceptable. The 2D interlayer FRET in the UTFs can be confirmed via a photoluminescence spectra ratio change from 1.48 to 0.88 between 475 and 600 nm (Fig. 3(b)). Moreover, 2D FRET can also be verified using the TRF of Znq_2 , with or without an acceptor MC molecule (Fig. 3(c)). The $(\text{Znq}_2\text{@PTBEM/LDH})_{16}$ UTF (Fig. S6 in the ESM) shows a double-exponential decay with an average lifetime of 20 ns at 475 nm. In the presence of MC@PTBEM , however, the TRF of $(\text{Znq}_2\text{@PTBEM/LDH/MC@PTBEM})_{16}$ UTF decays faster with an average lifetime of 15.5 ns, and a new decay time of $\tau_3 = 1.6$ ns (24%). This is attributed to FRET (Table S4 in the ESM). This result is similar to those shown in Fig. 1(d) and Table S1 in the ESM, and demonstrates the occurrence of 2D interlayer FRET.

Therefore, this device, which is without intra-micelle 0D FRET, proves that FRET can occur through the 2D interlayer, from $\text{Znq}_2\text{@PTBEM}$ to adjacent MC@PTBEM micelles, and across LDH nanosheets.

In this section, 2D FRET is realized by constructing 2D propagation medium with the aid of laminated LDH nanosheets, with an acceptable distance between the donor and acceptor. Meanwhile, 2D FRET can be turned off by introducing an intermediate layer (such as PSS) because of the increased distance between the donor and acceptor (Fig. S7 in the ESM).

3.3 Fabrication of $[(\text{Znq}_2/\text{MC})\text{@PTBEM/LDH}]_n$ UTFs and multi-dimensional FRET systems

According to the aforementioned work, an intra-micelle 0D FRET process using PTBEM micelles and 2D interlayer FRET using laminated LDH nanosheets have been demonstrated. With the development of multi-dimensional FRET in mind, a composite $[(\text{Znq}_2/\text{MC})\text{@PTBEM/LDH}]_{16}$ UTF was fabricated (Fig. 4(a)). The distance between two adjacent layers (d) is calculated to be ~ 9.8 nm from a low angle XRD pattern of $[(\text{Znq}_2/\text{MC})\text{@PTBEM/LDH}]_{16}$ UTFs (Fig. S8 in the ESM) via the Bragg equation $2d \sin \theta = n\lambda$ (d : interlaminar

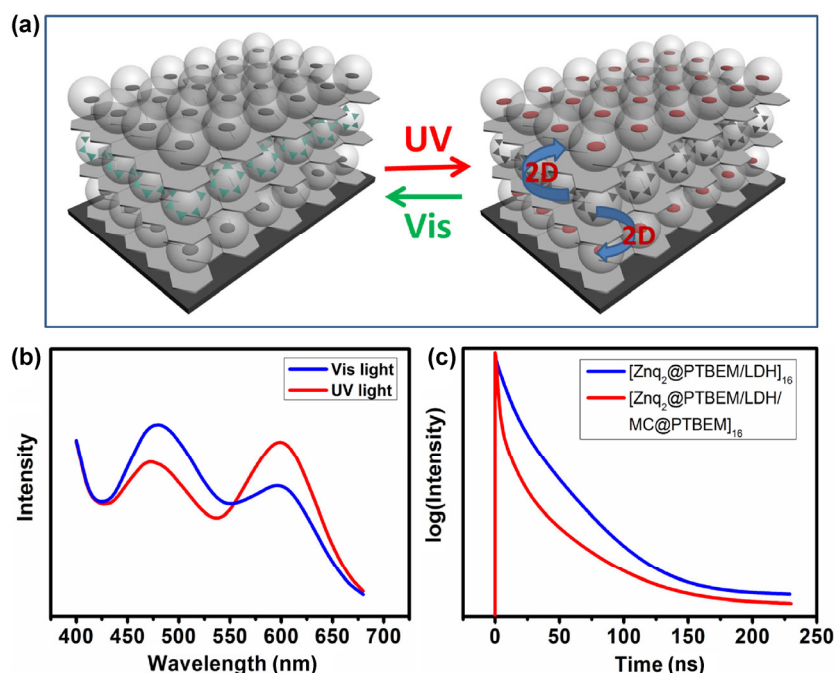


Figure 3 (a) Formation of an interlaminar 2D FRET system by assembling $\text{Znq}_2\text{@PTBEM}$ and MC@PTBEM with LDH nanosheets. (b) Photoluminescence spectra of $(\text{Znq}_2\text{@PTBEM/LDH/MC@PTBEM})_{16}$ UTFs triggered by UV and visible light. (c) Normalized TRFs of $(\text{Znq}_2\text{@PTBEM/LDH})_{16}$ and $(\text{Znq}_2\text{@PTBEM/LDH/MC@PTBEM})_{16}$ UTF at 475 nm.

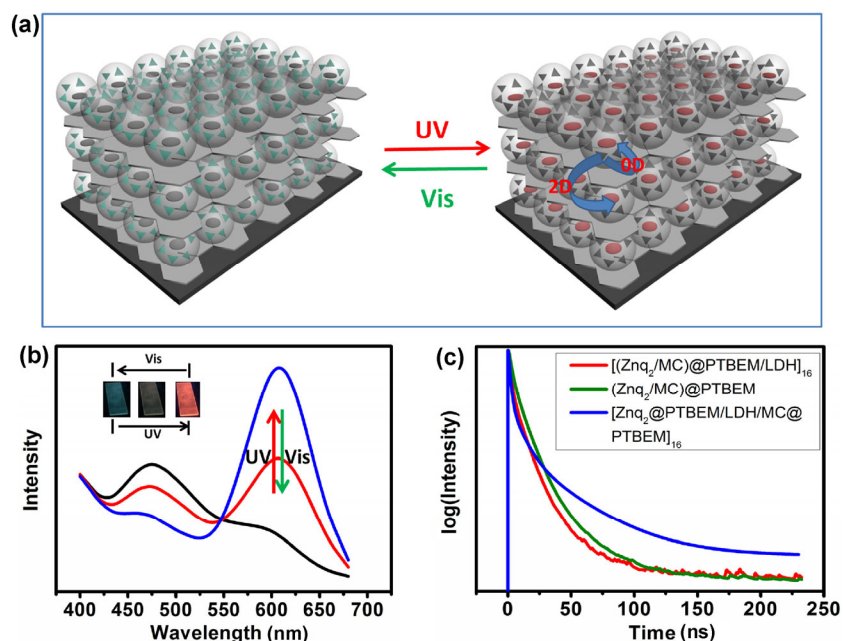


Figure 4 (a) Formation of intra-micelle 0D and interlamellar 2D FRET systems by assembling $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelles with LDH nanosheets. (b) Reversible fluorescent transformation of $[(\text{Znq}_2/\text{MC})@\text{PTBEM/LDH}]_{16}$ UTF induced by UV and visible light. (c) TRF of Znq_2 at 475 nm for $[(\text{Znq}_2/\text{MC})@\text{PTBEM/LDH}]_{16}$ UTF, $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ solution, and $[\text{Znq}_2@\text{PTBEM/LDH/MC}@\text{PTBEM}]_{16}$ UTF.

distance; $2\theta = 0.9^\circ$; $n = 1$; $\lambda = 0.154$ nm). Znq_2 and MC are encapsulated into the same micelle, which can exhibit 0D FRET from Znq_2 to MC in the same micellar core. Meanwhile, a multi-level UTF structure is built by assembling negative $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelles and positive LDH nanosheets. In this structure, fluorescent energy transfer from Znq_2 in one micelle to MC in another micelle across the LDH laminate occurs via a 2D propagation medium in the vertical direction. This UTF shows a reversible fluorescence transformation from blue to red, which is triggered by UV or visible light (Fig. 4(b)). Moreover, the TRFs from multi-dimensional FRET are displayed in Fig. 4(c). The composite of both 0D and 2D FRET (red line) shows the fastest decay with $\tau = 6.0$ ns (Table S5 in the ESM), which is faster than 0D FRET (green line, 7.1 ns) or 2D FRET alone (blue line, 15.5 ns). Moreover, the multi-dimensional FRET system exhibits a higher FRET efficiency (81.73%) than those of independent 0D (75.24%) and 2D (21.58%) systems (Table S5 in the ESM). In addition, obvious increases in the fluorescence lifetime (from 1.97 to 3.09 ns) and quantum yield (from 2.69% to 5.62%) of the receptor are obtained (Table S6 in the ESM). The distance between the donor

and acceptor is regarded as a key factor for FRET efficiency. Two explanations for this phenomenon have previously been reported: (i) elasticity between the donor and acceptor, and (ii) the binding effect between the donor and acceptor. Johnson et al. [49] reported that the FRET efficiency can be improved when an elastomer is compressed and decreased when it is stretched. In this work, the PTBEM micelle-encapsulating donor and the acceptor inside serve as a supermolecular elastomer, where the elasticity determines the donor–acceptor distance. This elastomer is compressed via immobilization in the interlayer region, relative to a free state in the liquid phase, which may result in enhanced FRET efficiency. The binding effect between the donor and acceptor is another factor which strengthens the FRET efficiency [50]. Herein, the exfoliated ultrathin LDH nanosheets are reconstructed as a 2D layered system with a donor and acceptor held on each side via electrostatic interactions, which may provide a beneficial binding effect that improves FRET efficiency.

The structural and morphological properties of $[(\text{Znq}_2/\text{MC})@\text{PTBEM/LDH}]_{16}$ were further studied. A top-down SEM image (Fig. 5(a)) shows a relatively

continuous and uniform surface. The side-view image reveals a thickness of ~ 157 nm (Fig. 5(b)). From this image, it is estimated that the average thickness of a bilayer repeat unit is 9.8 nm. This continuous, stacked structure confirms the successful construction of $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_{16}$ UTF. The distribution of organic and inorganic components in the material is shown by the EDX mapping of $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_{16}$ UTF (Fig. S9 in the ESM). Mg and Al from the LDH nanosheets show high density in the mapping, while Zn from Znq_2 has a lower density. The sources of C and N are complex, and include the donor (Znq_2), acceptor (MC), and PTBEM micelle. Overall, the main components (Mg, Al, Zn, C, N) of the material exhibit a uniform and well-proportioned distribution.

The typical photoresponsive behavior and reversibility of fluorescence modulation in $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_{16}$ UTFs via exposure to alternating cycles of UV and visible light are illustrated in Fig. 6. Upon irradiation with UV, multi-dimensional FRET causes the fluorescence intensity at 475 nm to gradually decrease over the course of 160 s. In contrast, it increases upon irradiation with visible light and returns to its maximum value after 140 s (Fig. 6(a)). Photostability

is an important criterion in practical applications of light-controlled FRET materials. The acceptor (MC) in the micelle is easily damaged by $^1\text{O}_2$ produced by UV irradiation [51], which leads to inactivation of the FRET system. The $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelle displays acceptable reversibility for 10 cycles and a marked loss after 15 cycles (Fig. S10 in the ESM). In contrast, the $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_{16}$ UTF shows better stability (Fig. 6(b)), which is due to the presence of the inorganic LDH framework. The FRET efficiency increases with irradiation by UV light (0%–81.73%), and then returns to $\sim 15.75\%$ after irradiation by visible light (Fig. S11 in the ESM), indicating that the efficiency of the multi-dimensional FRET system is highly tunable.

4 Conclusions

In conclusion, a multi-level $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_n$ UTF is designed and fabricated via LBL self-assembly with units of $(\text{Znq}_2/\text{MC})@\text{PTBEM}$ micelles and LDH nanosheets. The UTFs exhibit multi-dimensional, light-controlled FRET with the assistance of intra-micelle 0D FRET and interlayer 2D FRET with a donor–acceptor (Znq_2 –MC) pair. Multi-dimensional

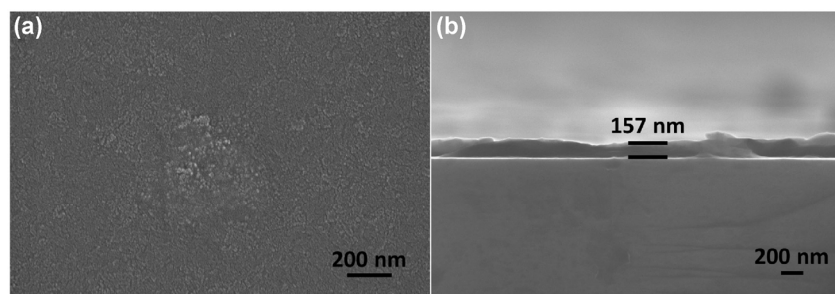


Figure 5 (a) Top-down SEM and (b) side-view image of $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_{16}$ UTFs.

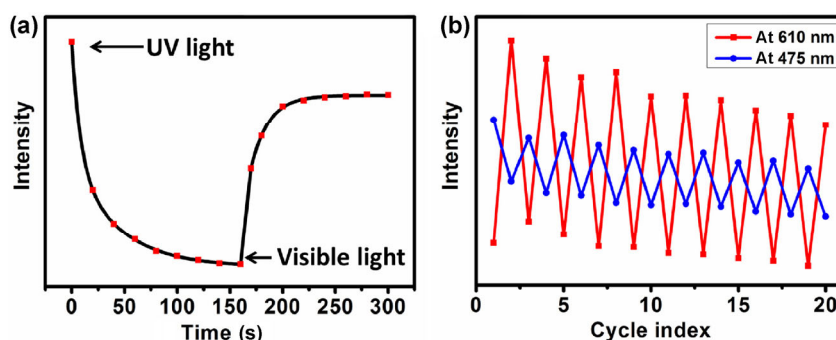


Figure 6 (a) Time dependence of the fluorescence intensity at 475 nm for $[(\text{Znq}_2/\text{MC})@\text{PTBEM}/\text{LDH}]_{16}$ UTF upon irradiation with UV, followed by visible light. (b) Reversibility tests recorded for the UTF at 475 and 610 nm, respectively.

FRET triggers a change in luminescent color between blue and red, which can be switched by alternating UV and visible light. This new multi-dimensional FRET system presents better energy transfer efficiency and time-dependent fluorescence emissions than systems that operate in only one dimension. This may lead to further exploration of optical detection, energy transmission, and optical memory. In addition, this fabrication method, which uses the assembly of 0D micelles with a 2D layered material can be extended to other systems to enable multi-dimensional FRET processes.

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Electronic Supplementary Material: Supplementary material (structural formula of materials, schematic diagram, UV/vis absorption and photoluminescence spectra of donor–acceptor pair, XRD, EDX mapping and a series of fluorescence lifetimes, FRET efficiency and quantum yields) is available in the online version of this article at <http://dx.doi.org/10.1007/s12274-016-1252-1>.

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