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ARTICLE TYPE

Lifetime-Ultra-Prolonged Luminescent Multilayer Thin Films with Electronic Microenvironment

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In this present report, luminescent multilayer thin films (MTFs) based on functional molecules intercalated into layered double hydroxides (LDHs) and montmorillonite (MMT) nanosheets were fabricated by layer-by-layer assembly method (LBL method). Exfoliated LDHs and MMT nanosheets with opposite charge can be expected to provide an electronic microenvironment (EME) for the chromophores which has not been found in the previous literatures, and to offer the inorganic rigid building blocks at the same time. Surprisingly, the lifetimes of MTFs with EME's architecture are significantly prolonged, compared with that of the pristine powder, even much longer than those of MTFs without EME's architecture. Therefore, it is highly expected that the EME formed by oppositely-charged inorganic nanosheets has remarkable influence on enhancing the lifetimes of chromophores, which suggests a new potential way to develop novel light-emitting materials and optical devices.

1. Introduction

Organic luminescent materials, due to their chemical stability and excellent luminescence properties, give rise to many possible applications in chemical sensors^{1,2}, optical devices³⁻⁷, photovoltaic cells^{8,9} etc. But compared with their solution counterparts, the luminescence performances of solid-state organic materials are still greatly limited by their poor optical stabilities and relatively short service lifetime¹⁰. For example, the phenomena of fluorescence red or blue shift, broadening, or even quenching, can still occurs in the solid state owing to the formation of aggregates of such species¹⁰⁻¹². Accordingly, the group of Tolbert used the oriented mesoporous silica composites to control the flow of energy transfer, which provide insights for optimizing nano-structured materials using in optoelectronic devices^{13, 14}, and then other scientists tried changing the external factors such as thermal and mechanical stimuli, to modify chemical structure of molecules for luminescent materials¹⁵⁻¹⁸.

Nowadays, layered materials are attractive targets for both fundamental research and practical application, for example layered double hydroxides^{19,20}, montmorillonite^{21,22}, perovskite oxides^{23,24}, and graphene^{25,26}, etc. As the successful liquid exfoliation of layered materials²⁷⁻²⁹ and the fruitful assembly of inorganic nanosheets³⁰⁻³², LBL method have been masterly used to build layered and ordered functional films. Recently, several groups have done many profound researches by using nanosheets with two-dimensional arrays which can provide a rigid and stable environment³³⁻³⁸. Especially, Duan *et al.* used LDHs nanosheets to suppress the chromophores' π - π stacking, and assembled well-oriented photoemissive structures with a macroscopic polarized optical effect³⁹⁻⁴². Various different inorganic nanosheets possibly contain a number of charges, such

as MMT's negative charge and LDHs' positive charge. Oppositely-charged nanosheets can be expected to form a nano-scaled capacitor providing an EME, which have no declaration in the previous literatures (Figure 1). Herein, what we are most interested in are whether functional molecules can be designed for intercalating into the oppositely-charged LDHs and MMT nanosheets, and how the EME affects on the properties of functional molecules.

In this work, a photoactive divalent cation bis(N-methylacridinium)(BNMA) was intercalated into the LDHs nanosheets and MMT nanosheets, using an optically-inert polyvinyl alcohol (PVA) as bonders for the purpose of fabricating MTFs (Figure 2). As the assembled nano-scaled capacitor can provide EME to the chromophores in the nano-system, the MTFs

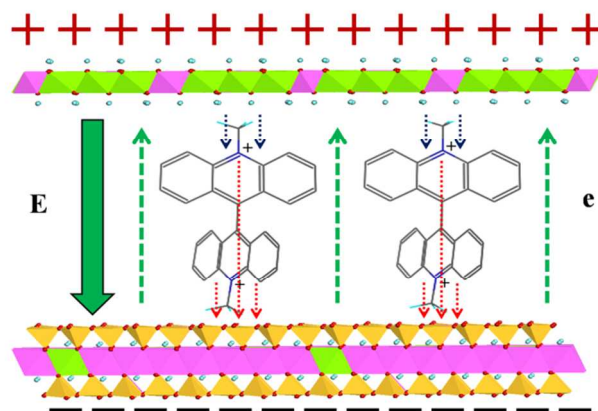


Figure 1. The sketch map of BNMA in EME between the MMT and LDHs monolayers. The green arrows indicate the EME's direction, the red show the repulsion of MMT nanosheets, and the dark blue show the attraction of LDHs nanosheets.

exhibit remarkable optical properties with reasonably longer luminescent lifetimes. Herein, this work successfully develops a general and facile method to fabricate novel inorganic-organic luminescent MTFs containing oppositely-charged nanosheets with a suitable and optically-inert polymer as the binder and puts forward a new concept about the nano-scale capacitor's effects on the chromophores.

2. Results and Discussion

The UV-visible absorption spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs with varying numbers of assembly steps are shown in Figure 3. The intensities of absorption peaks at 432nm exhibit correlate linearly with the layer number *n* (Figure 3, inset), which demonstrates a stepwise and regular growth procedure. Furthermore, the fluorescence

emission intensity at 510 nm also displays a consistent increase with *n*, as shown in Figure 4. Photoluminescence spectra of as-prepared MTFs with different layer number have no obvious red or blue shift, which implies the absence of BNMA aggregates throughout the whole assembly process.

To gain insight into the photophysical properties, the MTFs were studied by detecting luminescence lifetimes. Surprisingly, it is amazing that the lifetimes of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs are prolonged nearly 40-fold (13.81-17.02ns) (Table 1, Supporting Information FigureS1) compared with the pristine powder BNMA(0.37ns), and also are prolonged 3-fold compared with the LDHs/BNMA@PVS MTFs (4.61-4.88ns)⁴⁰. The remarkable increasing is partially due to the isolation effect (IE) imposed by the rigid LDHs and MMT monolayer, preventing the formation of chromophores

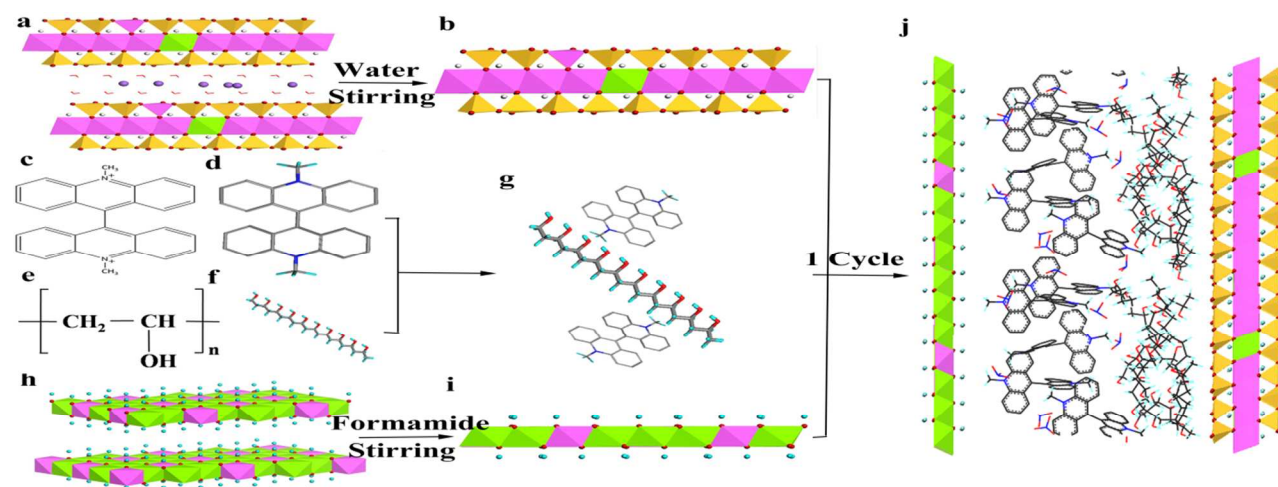


Figure 2. Assembly process of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs, a) A representation of MMT, pink: aluminium-oxygen octahedron, green: silicon-oxygen tetrahedron, yellow: magnesium-oxygen octahedron, b) The nanosheet of MMT, c) Chemical formula of BNMA, d) Structure of BNMA, e) Chemical formula of PVA, f) Structure of PVA, g) A representation of LDHs, pink: Al(OH)₆ octahedra, green: Mg(OH)₆ octahedra, i) The nanosheet of LDHs, j) The MTFs in 1 cycle.

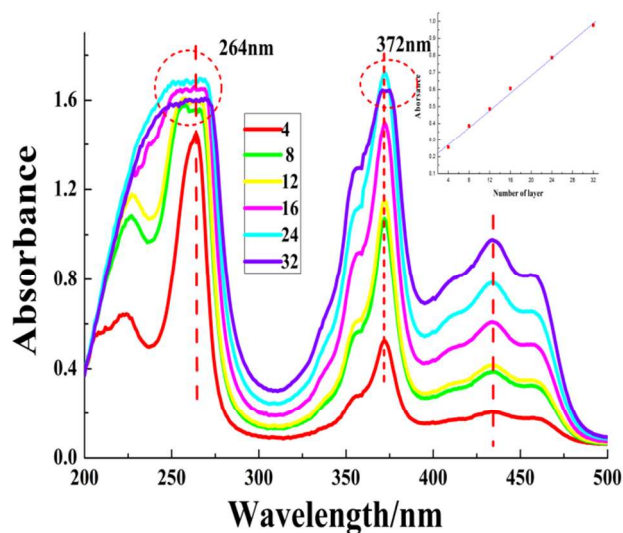


Figure 3. UV-visible absorption spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs. The inset shows the absorbance increasing linear relationship in 432nm.

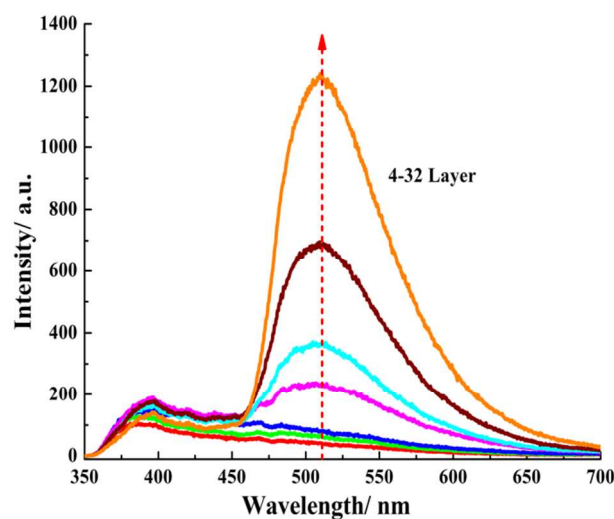


Figure 4. Photoluminescence spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs.

aggregation. But most importantly, positive charged LDHs and negative charged MMT nanosheets formed a nano-scaled capacitor, thus providing BNMA with an EME that could apparently affect the vibration of the valence electron of the chromophores which will definitely prolong their lifetimes. In order to verify this phenomenon, (MMT/BNMA@PVA)_n MTFs were fabricated in LBL method, and their lifetimes are shown in Supporting Information Table S2 and Figure S2. Combined with

Table 1. The summary of MTFs' lifetimes containing BNMA. τ_1 represents (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs' lifetimes, τ_2 represents (LDHs/BNMA@PVS)_n MTFs' lifetimes⁴⁰.

Layer number	8	16	24
Lifetime τ_1 (ns)	13.81	14.50	17.02
Lifetime τ_2 (ns)	4.61	4.83	4.88
$\tau_1/\tau_{01}^\ddagger$	37.34	39.21	46.00
τ_1/τ_2	3.00	3.00	3.49

the results of these MTFs' lifetimes, it is obvious that the lifetimes of MTFs are nearly in a stable growth but the (MMT/BNMA@PVA)_n MTFs' lifetimes increase linear more steeply. Furthermore, the (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs' lifetimes are obviously higher than (MMT/BNMA@PVA)_n MTFs' in the same cycles. According to this remarkable increase, the theory, as mentioned above, that EME can definitely prolong chromophores' lifetimes is reasonable. Figure 5 illustrates the comparison of chromophores' lifetimes in different states under different environments, and it is obviously that the chromophores under EME have amazingly ultra-prolonged lifetimes. Above all, these results can also be supported that the EME have remarkably effective influence on enhancing lifetime

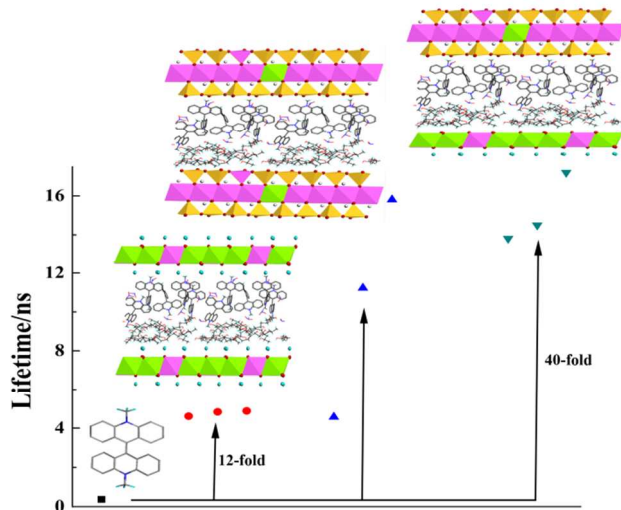


Figure 5. The comparison of chromophores' lifetimes in the different states under the different environments. Black dot represents the BNMA's lifetime, the red stand for the lifetimes of (LDHs/BNMA@PVS)_n MTFs, the blue represent the lifetimes of (MMT/BNMA@PVA)_n MTFs, and the dark green show the lifetimes of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs. IE is short for isolation effect, and EME is short for electronic microenvironment.

of the chromophores.

3. Experimental Section

3.1 Reagents and materials

All the chemicals are analytical grade and used as received without further purification. Bis(N-methylacridinium) (BNMA) and were purchased from Sigma Chemical. Co. Ltd, and polyvinyl alcohol (PVA, MW=1750) was purchased from Tianjin Fuchen Chemical Reagent Plant. Na-montmorillonite (MMT) was purchased from Zhejiang Sanding Co. Ltd. Mg(NO₃)₂•6H₂O, Al(NO₃)₃•9H₂O were all supplied by the Xilong Chemical Plant. NaOH, H₂O₂ (30%), H₂SO₄ (95%-98%) were supplied by the Beijing Chemical Reagent Company.

3.2 Characterization.

UV-visible absorption spectra were measured in the range from 200 to 500nm on a TU-1901 Double beam UV-vis spectrophotometer with slit width of 2.0nm. The fluorescence spectra were performed on F-4600 Fluorospectrophotometer. The fluorescence emission spectra are in the range from 350 to 700nm, and both the excitation and emission slit are set to 2.0 nm. The fluorescence decays and polarized photoluminescence measurements of MTFs were recorded by using an Edinburgh Instruments' Steady and transient time-resolved fluorescence spectrometer.

3.3 Fabrication of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs

An aqueous mixed nitrate solution (Mg/Al molar ratio equals 2.0) was prepared, and the concentration of Mg²⁺ is 0.8mol/L. The solution of sodium hydroxide (2.4mol/L) is mixed with the salt solution in the same rate under vigorous stirring. Then the suspension was stirred at 80°C for 24h under nitrogen gas flow. The precipitate was centrifuged, washed with hot distilled water and dried in a vacuum at 60°C.

The products (0.1g) of LDHs were mixed with 100mL formamide in a flask, which was tightly sealed after purging with nitrogen gas. The mixture was vigorously shaken by a mechanical shaker at a speed of 160rpm for 2 days. The upper suspension with exfoliated LDHs nanosheets were obtained after centrifugation at 10000rpm for 10 min. The MMT powder (1g) was dissolved in 1000mL distilled water. After vigorous stirring for 4 weeks, the insoluble fraction was allowed to deposit for 24 h and the suspension with exfoliated MMT nanosheets was collected for subsequent use. Quartz slides (1.5×1.5cm²) were cleaned in a "piranha" solution (H₂SO₄: H₂O₂=3:1 in volume), and then thoroughly rinsed with distilled water and dried under nitrogen flow. PVA was dissolved in distilled water to obtain 1wt% aqueous solution, the BNMA (1g) was dissolved in 100mL of distilled water, then the solution of BNMA and PVA were mixed (1:1 in volume) to form BNMA@PVA solution in which the concentration of BNMA is 0.5g/L. The heterogeneous thin films were fabricated by applying a cyclic repetition of the following steps: a) immersing the quartz slide into exfoliated MMT solution for 5 min, then thoroughly rinsing it with distilled water and drying it at room temperature; b) dipping it into an aqueous solution of BNMA@PVA for 5 min, then thoroughly rinsing it with distilled water and drying it at room temperature; c) dipping it into exfoliated LDHs suspension for 5 min, then

rinsing it with distilled water and drying it as mentioned above; d) dipping it into an aqueous solution of BNMA@PVA for 5 min, then followed by distilled water washing and drying it. All these procedures repeated n times to produce MTFs of (MMT/BNMA@PVA/LDHs/BNMA@PVA) $_n$.

3.4 Fabrication of (MMT/BNMA@PVA) $_n$ MTFs

The processes of fabrication of (MMT/BNMA@PVA) $_n$ is similar to (MMT/BNMA@PVA/LDHs/BNMA@PVA) $_n$, beside the aqueous nanosheets solution of MMT is absence.

10 Conclusions

To sum up, this work proposes a new method to assemble a novel luminescent MTFs with ultra-prolonged lifetime, as the chromophores were confined in the oppositely-charged inorganic layer hosts. It successfully demonstrates that the EME is fairly beneficial to enhancing the lifetimes of MTFs. Therefore, the as-fabricated MTFs are expected to have much flexibility and be potential for designing, constructing and investigating novel optoelectrical devices. Further work is ongoing with the research on lifetime of various luminescent guests imbedded in series of different LDHs/MMT nanosheets with EME.

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†Electronic Supplementary Information (ESI) available: Fluorescence lifetimes and Fluorescence lifetime and parameters of multi-exponential fit to the fluorescence decay of (MMT/BNMA@PVA/LDHs/BNMA@PVA) $_n$ MTFs; Polarized fluorescence spectra of (MMT/BNMA@PVA) $_n$ MTFs. See DOI: 10.1039/b000000x/

‡ τ_{01} represents the lifetime of the pristine powder BNMA, equaling to 0.37ns.

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