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Reply to Reviewers

Referee: 1

This is an interesting work with a DCM-based material to sense solvent polarity. I agree with referee 2 and 3 that there are some things unclear. The fluorescence spectra of compound DCM in different solvents should be given to interpret and evaluate the response of the materials to volatile organic solvent. Also, I am curious to know the responsive windows for different solvents.

Author reply: Thanks very much for your valuable suggestion. In ESI figure S1, various DCM solution (from hexane, toluene to DMF) show different luminescence, which is called luminescence solvatochromic effect. It is not a good sensor candidate for this solutions to probe VOCs, due to troublesome operation and irreversible probe. Furthermore, the drop-coating film of pristine DCM molecules was hardly emissive because of the severe aggregation-caused fluorescence quenching, so it is not available to study its response to VOCs.

We are not so sure about the meaning of “responsive windows”. If the “responsive windows” means “time windows”, our results indicated that the UTF fluorescence response to the VOC vapour immediately, maybe ca. 5 seconds. Many papers focus on the relaxation dynamics of DCM in solvent within picosecond transient scales, but it needs delicate instrument. We will further study this “responsive windows” of UTF to the VOC in the future.

Referee: 2

Comments to the Author

I believe this paper has gone through a very thorough review process with numerous questions raised and for the most part answered adequately. The authors produced several new data including further characterization Spherical micelle (Figure S2) and the repeat of the stability of UTF for the reversible photoluminescence response (Fig. 6B) etc.

The content of the manuscript is adequate for this journal and I support its publication as is. The only issue I can see is that the writing needs close grammatically corrections and edits. Even the starting sentence of "Over recently years, ..." is a bit awkward. The grammatical issues are the minor issues that require revision.

Author reply: Thank you very much for your valuable comments. We have checked the manuscript many times and make many grammatically corrections, marked by red in the revised manuscript.

Luminous Composite Ultrathin Films of DCM Dye Assembled with Layered Double Hydroxides and its fluorescence solvatochromism properties for polarity sensor

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In this work, neutral dye 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) incorporated by block copolymer micelle (BCM), poly(styrene-*b*-acrylic acid (PS-*b*-PAA), was assembled with layered double hydroxide (LDH) nanosheets to fabricate luminous ultrathin films by the layer-by-layer method. The UV-vis absorption spectra, SEM and AFM characterization results confirmed composite ultrathin films (UTFs) were homogenous with long-range ordered stacking vertical to quartz substrate. The UTFs maintained the photoluminescence (PL) properties of DCM with well-defined orange fluorescence which origin from the locally excited state of DCM without molecule aggregation. Meanwhile, these ultrathin films demonstrated typical solvatochromism fluorescent feature of DCM molecules, with the PL peak strongly dependent on solvent polarity. The fluorescence of the UTFs can be adjusted from orange to red by exposing in different volatile organic compounds (VOCs) vapours, based on the DCM twisted intramolecular charge transfer character-excited state. These DCM-loaded UTFs showed fast, sensitive and reversible fluorescence solvatochromism response to common VOCs. This work opens up the avenue for potential applications of DCM in the VOC polarity sensors.

1 Introduction

Over decades, organic light-emitting diodes (OLEDs) have attracted much academic and commercial attention because of their tremendous applications in full-color displays.^{1,2} 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylamino styryl)-4H-pyran (DCM)-type dye is one of the most efficient materials among the existing synthesized and studied red fluorescence dyes for OLED and dye lasers.^{3,4} However, most red fluorescence dyes were tended to aggregate in solid state and become weakly emissive or even quenched, as a result of either intermolecular π -stacking or dipole-dipole interactions.⁵ Therefore, red fluorescent materials are less flexible and mostly confined to use as doping materials in the fabrication of flat panel display applications, compared with blue- and green-light-emitting materials. Practically, many efforts have been made to solve the problem of concentration quenching of red materials, such as doped in tris(8-quinolinolato) aluminum (Alq₃) or rubrene,^{6,8} incorporated sterically bulky moieties into the red dyes to

prevent exciplex formation.⁹⁻¹¹ Nevertheless, these methods require complex synthetic procedures and time-consuming, so it is desired to find facile ways to alleviate the concentration quenching.

Moreover, the DCM molecules exhibit the luminescence solvatochromic effect due to its existing strong electron donor group (*p*-dimethylamino styryl), and electron acceptor group (4-dicyanomethylene pyran). Solvatochromic fluorophores exhibit emission properties, such as fluorescence wavelength, lifetimes, and quantum yields, were highly sensitive to the dielectric nature of local microenvironment, resulting from their unique molecular structures with electron donor-acceptor (D-A) characters. Solvatochromic fluorophores can show various Stokes shifts in polar solvents due to the charge transfer between terminal electron-donating and electron-accepting groups, which can be used as a probe to detect different solvents.¹²

Layered double hydroxides (LDHs) are one significant type of functional layered inorganic materials, and are generally expressed by $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are metal cation and A^{n-} is the

interlayer anion. LDHs can be exfoliated into positively-charged nanosheets and used as building blocks to assemble with anionic substance to construct various inorganic/organic composite films via the layer-by-layer (LbL) assembly method.¹³ Block copolymer micelles (BCMs) can form unique core-shell micellar architecture in aqueous solution resulting from their hydrophilic and hydrophobic segment, such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA). Therefore, BCMs possess great potential for incorporating hydrophobic species into the hydrophobic interior of micelles, such as fluorescent dyes,¹⁴ organic capped gold,¹⁵ magnetic nanoparticles¹⁶. More recently, there have been several reports about LbL assembly of negatively-charged micelles with polyelectrolytes.¹⁷

Herein, an ultrathin film (UTF) was fabricated by the assembly of block copolymer micelles (PS-*b*-PAA) encapsulating neutral DCM molecules and LDH nanosheets by the electrostatic LbL method, which realized the immobilization of DCM molecules in the two-dimensional LDH interlayer without degrading its fluorescence properties. The SEM, AFM and small-angle XRD measurements indicated that the composite films are homogeneous, smooth, and long-range ordered, with a periodic repeating distance of ~9 nm in the normal direction. The composite films exhibited variable fluorescence color (from 550 to 600 nm) by exposing to various solvent vapours, which provided a simple route to fabricate the fluorescence polarity sensor for volatile organic compounds (VOCs).

2 Experimental

2.1 Reagents and Materials

4-(Dicyanomethylene)-2-methyl-6-(4-dimethylamino-styryl)-4H-pyran, (DCM, C₁₉H₁₇N₃O, M_w = 303.36, 98%) was purchased from Sigma Chemical. Co. Ltd. Amphiphilic diblock copolymer (poly(styrene-*b*-acrylic acid, M_n PS(12000)-PAA(1100), M_w/M_n = 1.10, PS₁₁₅-PAA₁₅) was purchased from Polymer Source Inc. Analytical grade including NaNO₃, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, urea, tetrahydrofuran (THF), formamide, acetone, chloroform, toluene, pyridine, N, N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), H₂SO₄ and H₂O₂ were bought from Beijing Chemical Co. Ltd. All these reagents were used without further purification. Deionized water was used in all the experimental processes.

2.2 Preparation of PS-PAA@DCM micelle solution

The DCM and PS-PAA solution were prepared by dissolving DCM in DMF solvent (0.5 g·L⁻¹) and PS-PAA in water (containing 4% DMF, 0.32 g·L⁻¹), respectively. The DCM@PS-PAA micelle solution was obtained as follows: 20-200 μL DCM solution were added into 10 mL PS-PAA solution and ultrasonic

treating for 30 min, the final DCM concentrations were 1, 3, 5, 7, 10 mg·L⁻¹, respectively. The pH value of the final micelle was adjusted to 10 by 1 M NaOH solution.

2.3 Fabrication of (PS-PAA@DCM/LDH)_n UTFs

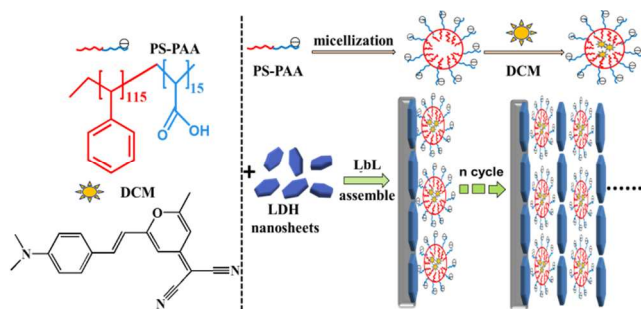
The process of synthesis and exfoliation of Mg₂Al-LDH was similar to that reported in the previous work.¹⁸ 0.1 g Mg₂Al-LDH was ultrasonically shaken in 100 mL formamide solution for 24 h to produce a colloidal suspension of exfoliated MgAl-LDH nanosheets (1 g·L⁻¹). The quartz substrate was first cleaned in H₂SO₄/H₂O₂ (vol/vol = 7:3) (*caution: piranha solution is extremely corrosive*) for 30 min and then washed by deionized water thoroughly. The cleaned substrates were dipped into the DCM@PS-PAA micelle for 10 min followed by washing thoroughly, and then dipped into the LDH nanosheets colloidal suspension for 10 min and washed thoroughly by deionized water. The (DCM@PS-PAA/LDH)_n multilayer UTFs were fabricated by the alternately depositing DCM@PS-PAA micelle and LDH nanosheets suspension for *n* cycles. For comparison, the pristine DCM@PS-PAA drop-coating films were prepared by solvent evaporation method.

2.4 Characterization.

The small-angle X-ray diffraction patterns (XRD) of the films were recorded using a Rigaku 2500VB2+ PC diffractometer under the following conditions: 40 kV, 50 mA, and Cu Kα radiation (λ = 1.541844Å) with step scanning (0.04°/2θ per step) in the range from 0.5 to 8° using a count time of 10 s/step. The morphology and thickness of thin films were investigated by using a scanning electron microscope (SEM Zeiss Supra 55) and the accelerating voltage applied was 20 kV. The surface roughness data of the UTFs were obtained by using the atomic force microscope (AFM) software (Digital Instruments, Version 6.12). The UV-vis absorption spectra were collected in the range from 200 to 700 nm on a Shimadzu U-3600 spectrophotometer with the slit width of 1.0 nm. The steady state fluorescence excitation and emission spectra were performed on a RF-5301PC fluorospectrophotometer, and both the excitation and emission slit are set to 3.0 nm, with the excitation at 488 nm, and a PMT voltage of 400 V. The fluorescence decay curves were recorded with an Edinburgh Instruments' FLS980 fluorimeter with the excitation at 488 nm from the H₂ lamp (40 kHz) and recorded by the time-correlated single photon counting detector. The weighted average fluorescence lifetime were obtained by the multiple-exponentially fitted the decay curves with the Edinburgh F980 instruments software.

3 Results and discussion

3.1 Assembly of the (PS-PAA@DCM/LDH)_n UTFs



Scheme 1 Molecular structure of PS-*b*-PAA and DCM, and process scheme of formation of PS-*b*-PAA@DCM micelle and LbL fabrication of (PS-*b*-PAA@DCM/LDH)_{*n*} film.

It is well known that the PS-*b*-PAA block copolymer can self-organize into core/shell structure in water, so the physical encapsulation of DCM within the hydrophobic core of PS-*b*-PAA with hydrophilic shell makes DCM dye dispersion uniform in aqueous media. In the alkaline condition (pH = 10), the negative-charged micelle and the positive-charged LDH nanosheets were deposited on the quartz substrate by electrostatic LbL assembly, and the UTFs as more as 50 bilayers can be fabricated by the alternately deposition of BCM and LDHs nanosheets. Scheme 1 shows the formation of PS-*b*-PAA@DCM micelle and the multilayer assembly process of PS-*b*-PAA@DCM/LDH UTFs. The fluorescence spectrum of DCM initial solution (5 mg·L⁻¹) consists of a strong broad band photoemission peaking near 465 to 630 nm, in various solvents from methanol to DMF (Fig. S1, ESI†). The as-prepared PS-*b*-PAA@DCM micelle showed clear Tyndall light scattering and orange fluorescence under 365 nm UV light (Fig. S2). The micelle exhibited a fluorescence band at 560 nm, while that of the UTFs and drop-coating films blue-shifted slightly to 551 nm, which was similar to that of DCM doping in PMMA matrix reported elsewhere.¹⁹ When doped in solid matrices, the C-C bond rotation of DCM is restricted, the fluorescence at 550 nm originated from the locally excited state of DCM. The DCM concentration in micelle was studied and the optimal concentration was 5 mg·L⁻¹ with the fluorescence of DCM was maintained (Fig. S3). It is reasonable that the emission intensity of DCM increased with the increasing DCM concentration at a small loading ratio, but if the concentration was too high, many of the DCM molecules tended to form aggregates and fluorescence fell severely. It is noted that the PL emission peak showed a spectral bathochromic shift when DCM concentration increased in the doping system,¹⁹ but the red-shift did not occur in the BCM micelle, which may be ascribed to the DCM dispersed homogeneously in the hydrophobic core of BCM. Therefore, the DCM concentration of 5 mg·L⁻¹ was used to build the PS-*b*-PAA@DCM/LDH UTFs.

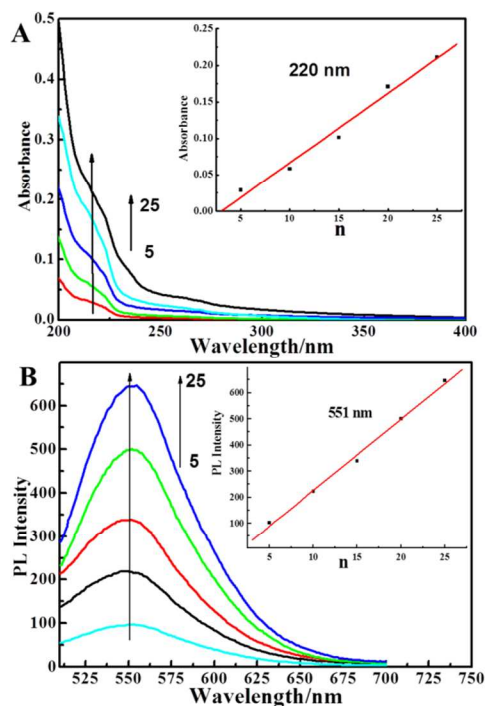


Fig. 1 (A) UV-vis absorption and (B) photoemission spectra of (PS-PAA@DCM/LDH)_{*n*} UTFs (*n* = 5-25) excited by 488 nm, optimal excitation wavelength of DCM. The insets in panel A and B showed the plot of the absorbance and photoemission at 220 nm and 551 nm vs *n*, respectively.

The UV-vis absorption spectra and fluorescence spectra were used to monitor the growth of the fabricated films. The absorption band at ~220 nm is characterized by the π - π^* transition of the phenyl ring in PS block and the absorption increased linearly with the bilayer number *n* (Figure 1A), indicating the films were LbL linearly grown. The intensity of the fluorescence maximum at 551 nm displays well-defined orange fluorescence and monotonic increase vs *n* (Figure 1B), which further confirmed these UTFs were uniformly linearly deposited. The absorbance and fluorescence results indicated that film growth process was regular and stepwise, and the assembled micelle dispersed homogeneously within the interlayers of LDH by the electrostatic interaction, and surmount the serious aggregation-caused fluorescence quenching of DCM.

3.2 Structural and Morphological Characterization of (PS-PAA@DCM/LDH)_{*n*} Assembly UTFs

The alternative deposition of PS-PAA@DCM micelle and LDH nanosheets by electrostatic interaction would lead to a periodic orderly hybrid film stacked with the ab-plane of LDH nanosheets lying in the substrate. The SEM and AFM measurements were used to examine the thickness and surface morphology of PS-PAA@DCM/LDH UTFs.

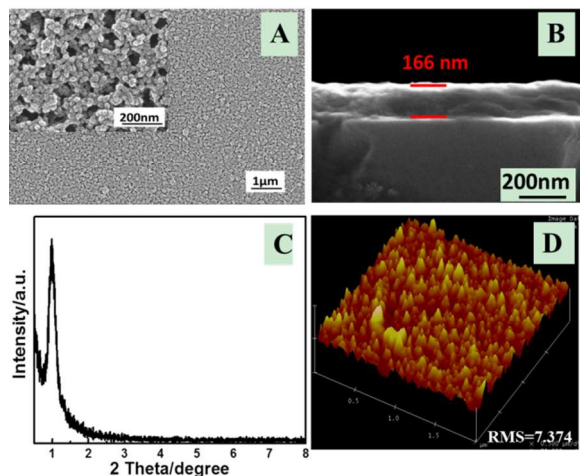


Fig. 2 Morphology characterization of UTF-20: (A) top-view SEM image, the inset is the enlarged image; (B) side-view SEM image; (C) small-angle XRD pattern; (D) tapping-mode AFM image.

The SEM image of the colloidal solution showed the micelle is dispersive spherical shape with the uniform diameter around 30 nm (Fig. S2). The top-view image (Fig. 2A) displays the UTFs were continuous, homogenous, and the inset image shows the micelle shape was maintained. The side-view SEM image showed the thickness of UTFs increased gradually with the increasing bilayer number (Fig. 2B, Fig. S4). The approximately linear increase of thickness as a function of n was displayed and thus the average UTFs thickness can be estimated to ~ 9.35 nm per bilayer cycle. Small-angle XRD measurement was performed to check the period structure of composite film and revealed that the UTFs were significantly ordered along the normal with a strong Bragg peak at $0.97^\circ(2\theta)$, corresponding to a spacing of about 9.0 nm, consistent with that of the side-view SEM results (Fig. 2C). The AFM image ($5\mu\text{m}\times 5\mu\text{m}$) of UTFs-20 was shown in Fig. 2D, and the value of root-mean-square (RMS) roughness was found to be 7.374 nm, indicating a relatively smooth surface of these UTFs. The RMS roughness values for the composite films increases gradually from 3.907 to 9.182 nm as the bilayer number varies from 5 to 20 (Fig. S5). These results confirm the UTFs fabricated by LbL assembly were long-range ordered and homogeneous, consistent with the optical absorption and fluorescence results.

3.3 Fluorescence Lifetime and Fluorescence Polarization of the (PS-PAA@DCM/LDH) $_n$ UTFs

To further understand the influence of PS-PAA BCM and LDH nanosheets on the photoluminescence properties of DCM molecules, DCM DMF solution ($5\text{ mg}\cdot\text{L}^{-1}$), PS-PAA@DCM micelle solution and PS-PAA@DCM/LDH UTF-20 were studied by detecting their fluorescence decay. The UTFs exhibited increased fluorescence lifetime compared with the DCM DMF

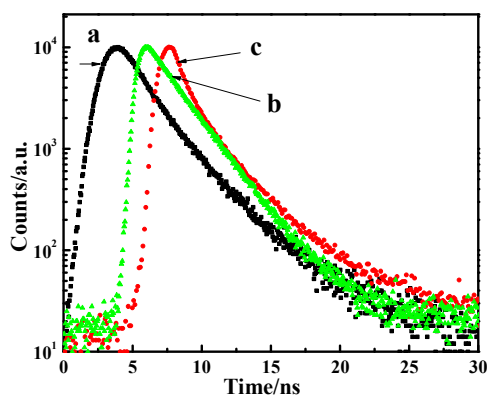


Fig. 3 The fluorescence decay curves of DCM DMF solution (612 nm) (a); PS-PAA@DCM micelle solution (560 nm) (b) and PS-PAA@DCM/LDH UTF-20 (551 nm) (c), excited by 488 nm.

solution and PS-PAA@DCM micelle solution (Fig.3). Figure 3 shows the radiative decay profiles collected at the DCM maximum emission for DMF solution (612 nm), micelle (560 nm) and hybrid film (551 nm) under DCM maximal excitation of 488 nm. All of the DCM decay curves were well-fitted by bi-exponential function, indicating that there were two relaxation pathways in the decay process (fast (τ_1) and slow (τ_2)), and their τ_1 and τ_2 values are reported in Table S1. The photoluminescence of DCM dye decays slower in the hybrid thin film state than in the DMF and micelle solution, for example, the fluorescence lifetime of DCM in the film and in the DMF and micelle solution were 2.23 ns, 1.66 ns and 1.88 ns, respectively. The longer fluorescence lifetime maybe the result of the homogeneity dispersion of DCM molecules in the PS-PAA BCMs and the immobilization of PS-PAA@DCM micelle in the LDH host interlayer, thus suppressed the concentration quenching of DCM. Furthermore, the decay profile was somewhat different for DCM DMF solution and DCM micelle (solution or UTFs), in that there existed about 3 ns silence time in the initial decay before reaching their fluorescence maximum for the latter, which indicated that different excitation state involved in the decay process, and maybe related with the locally excited (LE) state for the latter and twisted intramolecular charge transfer character (TICT) state for the former. While the fluorescence lifetime of the amorphous PS-PAA@DCM drop-coating film was too short to be detected (not shown) because of the severe aggregation-caused fluorescence quenching.

It has been reported the assembly films based on LDHs could achieve enhanced fluorescence anisotropy.²⁰ Thus, anisotropic photoluminescence spectroscopy was performed to investigate the orientation of DCM molecules in the DMF solution, micelle and PS-PAA@DCM/LDH UTF-20. The anisotropic value r is used to evaluate the fluorescence polarization of materials.²¹ It can be expressed as follows: $r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH})$, where $G = I_{HV} / I_{HH}$. In the above formula, I_{VH} represents the photoluminescence intensity obtained with vertical excitation and horizontal detection, and I_{VV} , I_{HV} , and I_{HH} are defined in a similar manner.

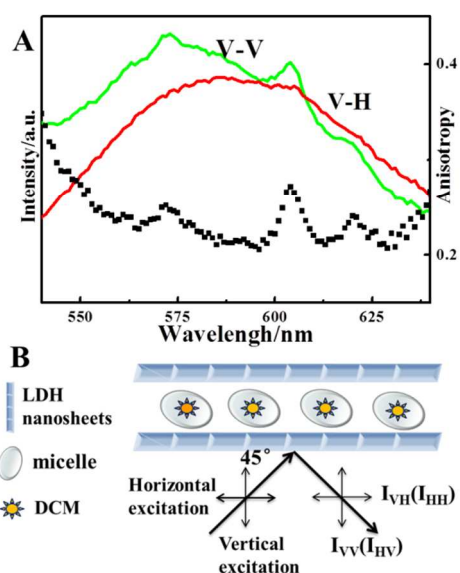


Fig. 4 (A) Polarized luminescence profiles for the VV and VH modes and anisotropic value (r) for UTF-20, with the optimum excitation wavelength of 488 nm; (B) Schematic diagram of fluorescence polarization measurements with excitation light from 45° incident geometry for the UTF.

Theoretically, the anisotropic value r varies from -0.2 (absorption and emission transition dipoles are perpendicular) to 0.4 (two transition dipoles are parallel). In contrast to the DCM DMF solution with low luminescence polarization ($r=0.01$), the PS-PAA@DCM micelle and PS-PAA@DCM/LDH UTF-20 achieved much improved anisotropy r of about 0.17 and 0.25 , respectively, in the range of 500 to 600 nm for the orange photoluminescence (Fig. 4, Fig. S6). These enhanced luminescence polarization indicated the improvement in the overall orientation of the DCM molecules in the micelle and being well-organized between the LDH monolayers. It can be reasonably speculated that, on the one hand, the DCM molecules were confined in the hydrophobic core of PS-PAA BCMS, on the other hand, the interaction between the host-guest induces the PS-PAA@DCM micelle to arrange in a certain orientation (Fig. 4B). These may be the cause of the enhanced polarized photoemission. The micelle-encapsulated DCM molecules immobilized by the LDH in the hybrid films acquired not only prolonged fluorescence lifetime but also raised luminescence anisotropy value r .

Table 1. Spectroscopic properties of the UTFs in organic solvents of different polarity

Solvent	ϵ^a	$E_T(30)^b$	$\lambda_{\max}/\text{nm}^c$	$\Delta\lambda/\text{nm}$
Toluene	2.38	33.9	557	6
THF	4.81	37.4	565	14
CHCl_3	7.52	39.1	575	24
Pyridine	12.9	40.5	588	37
DMSO	46.6	45.1	599	48

Note: ^a The solvent dielectric constant. ^b The polarity index taken from ref. 23. ^c The maximum emission wavelength.

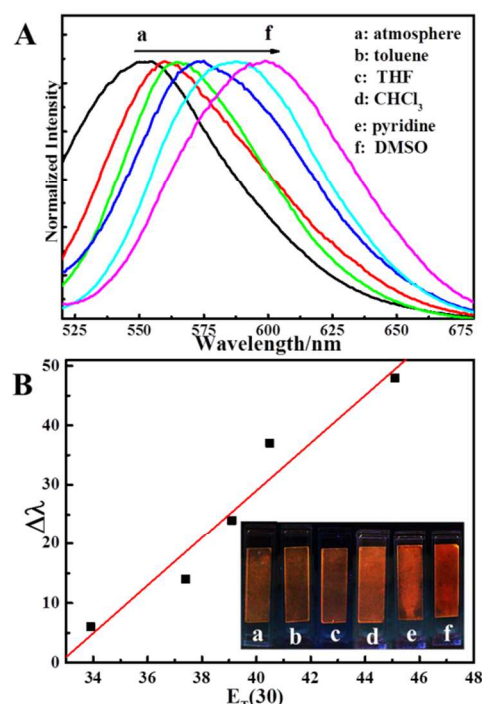


Fig. 5 Fluorescence solvatochromism properties of UTF-20: (A) normalized fluorescence spectra of UTF in organic solvent vapours with different polarity for 488 nm excitation; (B) solvatochromic fluorescence shifts of DCM versus the polarity $E_T(30)$ value. Inset: photograph of UTF-20 in different solvents under UV lamp of 365 nm.

3.4 Reversible Photoluminescence Response to the VOC polarity

Many of the intriguing optical properties of DCM resulted from the charge transfer in the excited state formed by charge separation between the electron-donating group and the electron-accepting group. The molecule exhibits a large solvent-polarity-dependent Stokes shift in fluorescence due to the considerable charge separation. Since different polar solvents can influence the electronic structure of DCM molecule, it is interested to study whether the incorporated DCM molecules could still hold the fluorescence solvatochromism properties after inserting into the LDH interlayer. For this purpose, the DCM-loaded UTF-20 was exposed in an airtight quartz cell full of certain VOC vapours (toluene, chloroform (CHCl_3), tetrahydrofuran (THF), pyridine, dimethyl sulfoxide (DMSO)). Then, the UTFs were recorded by fluorescence spectroscopy immediately. It turned out that the hybrid films exhibited sensitive solvatochromism and large Stokes shifts when adsorbed different VOC vapours. For example, the fluorescence emission of DCM with 488 nm excitation could be modulated from 551 nm to 600 nm, in different polar solvent vapour from toluene to DMSO. Fig. 5A depicts the fluorescence spectra of UTFs-20 in different VOCs, which demonstrated that the DCM photoemission wavelength increased dramatically with increasing solvent polarity. Table 1 revealed the details of change in

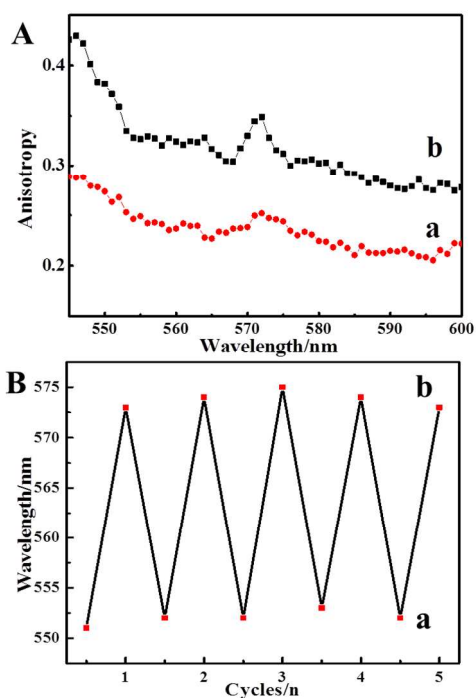


Fig. 6 (A) Fluorescence anisotropic value (r) and (B) the reversible fluorescence response of five consecutive cycles of the UTF in the atmosphere (a) or exposure to CHCl_3 vapour (b).

emission wavelength with the increasing solvent polarity. The VOC induces a large charge transfer in the excited state, which induced the redshift luminescence of DCM to different extent in different polar solvents. Similar results about the change of DCM electronic structure strongly dependent on the solvents have been reported before.²² Subsequently, the correlation of redshift ($\Delta\lambda$) of the composite films with the polarity index $E_T(30)$ was studied.²³ A good linear correlation was observed with the goodness of fit, $R^2 = 0.9896$, as shown in Fig. 5B. The largest redshift $\Delta\lambda$ (48 nm) was observed for DMSO with $E_T(30) = 45.1$. It can be seen clearly from the inset photograph of Fig. 5B that the colour of the hybrid films changed from orange to red in various solvents under UV lamp. Such a fluorescence redshift observed for hybrid films in the vapour of organic solvents can be ascribe to the fact that the TICT state is preferable and no emission from the LE state was observed.⁴ Transition to the TICT conformation takes place from the plane "untwisted" molecule of local excited state, and wherein each conformation corresponding to specific fluorescence spectrum. The TICT excited state was preferred in polar environment, while the local excited state was stable in non-polar environment. Furthermore, the solvent vapour enabled the anisotropic value (r) of the UTF increasing from 0.25 (in atmosphere) to 0.35 (in CHCl_3 vapour) (Fig. 6A), maybe the TICT conformation makes interlayered DCM molecules tend to adopt an enhanced well-organized structure between the LDHs gallery.

Intriguingly, this fluorescence solvatochromic shift towards to solvent can be recovered when the solvent

desorbed from the films by drying at 60 °C in vacuum and repeated upto five times. Fig. 6B demonstrated the ultrathin film was reversible and stable when underwent five consecutive cycles in the atmosphere or exposure to CHCl_3 vapour. On the contrary, the drop-coating pristine PS-PAA@DCM films show confused and overlapped emission spectra and poor reversibility when exposed to the solvent vapours (Fig. S7). This obvious difference of fluorescence spectra between the UTF and PS-PAA@DCM drop-coating films may be owing to the ordered structure of the ultrathin films and the homogeneity dispersion of PS-PAA@DCM in the confined 2D LDH host interlayer. Therefore, these ordered 2D composite films could exhibit two fluorescence signals corresponding to the VOCs' adsorption or desorption status, and this conversion is reversible and fast which is necessary for polarity sensor. The unique molecular structure of DCM with electron donor-acceptor characters endows DCM with a TICT excited state, compared to the neutral ground state, affected by the ambient solvent molecules. TICT states generally lead to a broad-band and red shifted emission and thus the UTF fluorescent emission shifts to the red wavelength in polar VOCs. Based on the layered assembly configuration of the UTF, it can be speculated that the VOC molecules first penetrated into the hydrophobic interlayer space of the LDHs and then the hydrophobic core of PS-PAA BCMs, thus the VOC molecules formed an environment with some polarity in the periphery of DCM molecules, and stabilized the TICT state to some extent when light excitation. The confine environment of PS-PAA BCM and 2D LDH interlayer limited the CT states of DCM, inducing the bathochromic solvatochromism and redshifts. As the DCM TICT excited states in polar solution formed within the range of picosecond transient,²⁴ so the redshifts can be detected immediately by the luminescence spectroscopy without waiting for the balance time.

For VOC detection, the PS-PAA@DCM/LDH UTF exhibited different fluorescence spectrum toward the polar VOCs, and this makes it possible to recognize VOC by probing polarity. Therefore, these observations clearly attest that the PS-PAA@DCM/LDH UTFs provide a convenient and reversible approach to detect the polarity of VOCs by fluorescence redshift and can be used as polarity sensor.

4 Conclusions

In summary, a simple and feasible method has been developed to fabricate the ultrathin film based on micelle (PS-*b*-PAA) incorporated neutral molecules (DCM) assembled with inorganic LDHs nanosheets to immobilize the DCM molecule and maintain its fluorescence properties. The structural and surface morphology investigation revealed that the composite film is continuous and uniform with long-range ordered stacking vertical to quartz substrate. The DCM molecules

encapsulated in the LDHs interlayer exhibited non-aggregating fluorescence behavior, and acquired prolonged fluorescence lifetime and increased luminescence anisotropy value. These DCM@PS-PAA/LDH composite UTFs exhibited fast, reversible fluorescence response to various polar solvents, and the fluorescence bathochromic shift was sensitive for polarity of VOCs with the peak shifted within 550 (in toluene) to 600 nm (in DMSO). Therefore, these UTFs can be found potential application in the polarity sensor for VOCs. Some of the key factors remain to be studied further, such as the interaction between BCM and DCM, BCM and LDH nanosheets.

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Notes and references

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†Electronic Supplementary Information (ESI) available: fluorescence spectra of DCM in different solvents; structural and optical characterizations of PS-PAA@DCM micelle; fluorescence spectra of (PS-PAA@DCM/LDH)_n UTFs with different incorporated DCM concentrations; side-view SEM images and tapping-mode AFM images of UTFs with different bilayers; fluorescence lifetime of UTF-20 and PS-PAA@DCM micelle; polarized luminescence profiles of DCM DMF solution and PS-PAA@DCM micelle solution; normalized fluorescence spectra of pristine PS-PAA@DCM drop-coating films in different organic solvent vapours. See DOI: 10.1039/b000000x/.

- C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
- C. W. Tang, S. A. VanSlyke and C. H. Chen, *Appl. Phys. Lett.*, 1989, **65**, 3610.
- M. L. Horng, J. Gardecki, A. Papazyan and M. Maroncelli, *J. Phys. Chem.*, 1995, **99**, 17311.
- J. C. Mialocq and M. Meyer, *Laser Chem.*, 1990, **10**, 277.
- C. H. Chen, *Chem. Mater.*, 2004, **16**, 4389.
- Z. Y. Xie, L. S. Hung and S. T. Lee, *Appl. Phys. Lett.*, 2001, **79**, 1048.
- J. Feng, F. Li, W. Gao, G. Cheng, W. Xie and S. Liu, *Appl. Phys. Lett.*, 2002, **81**, 2935.
- T. H. Liu, C. Y. Iou and C. H. Chen, *Appl. Phys. Lett.*, 2003, **83**, 5241.

- Y. Hamada, *IEEE Trans. Electron Devices*, 1997, **44**, 1208.
- L. S. Hung and C. H. Chen, *Mater. Sci. Eng. R*, 2002, **39**, 143.
- Y. S. Yao, J. Xiao, X. S. Wang, Z. B. Deng and B. W. Zhang, *Adv. Funct. Mater.*, 2006, **16**, 709.
- (a) M. A. Fakhari and S. E. Rokita, *Chem. Commun.*, 2011, **47**, 4222; (b) Y. Zhang, D. Li, Y. Li, and J. Yu, *Chem. Sci.*, 2014, **5**, 2710; (c) Y. Niko, S. Kawachi and G. Konishi, *Chem. Eur. J.* 2013, **19**, 9760; (d) A. Goel, V. Kumar, S. P. Singh, A. Sharma, S. Prakash, C. Singh and R. S. Anand, *J. Mater. Chem.*, 2012, **22**, 14880; (e) R. W. Sinkeldam, N. J. Greco and Y. Tor, *Chem. Rev.*, 2010, **110**, 2579.
- (a) Z. P. Liu, R. Z. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 4872; (b) D. Yan, J. Lu, M. Wei, J. Ma, D. G. Evans and X. Duan, *Chem. Commun.*, 2009, 6358; (c) C. A. Antonyraj, P. Koilraj and S. Kannan, *Chem. Commun.*, 2010, **46**, 1902.
- S. Li, J. Lu, H. Ma, D. Yan, Z. Li, S. Qin, D. G. Evans and X. Duan, *J. Phys. Chem. C*, 2012, **116**, 12836.
- (a) Y. Kang and T. A. Taton, *Angew. Chem., Int. Ed.*, 2005, **44**, 409; (b) Y. Kang, K. J. Erickson and T. A. Taton, *J. Am. Chem. Soc.*, 2005, **127**, 13800.
- B. S. Kim, J. M. Qiu, J. P. Wang and T. A. Taton, *Nano Lett.*, 2005, **5**, 1987.
- (a) N. Ma, H. Zhang, B. Song, Z. Wang and X. Zhang, *Chem. Mater.*, 2005, **17**, 5065; (b) B. S. Kim, S. W. Park, and P. T. Hammond, *ACS Nano*, 2008, **2**, 386.
- J. B. Han, J. Lu, M. Wei, Z. L. Wang and X. Duan, *Chem. Commun.*, 2008, **41**, 5188
- S. Toffanin, R. Capelli, T. Y. Hwu, K. T. Wong, T. Plötzing, M. Först, and M. Muccini, *J. Phys. Chem. B*, 2010, **114**, 120.
- (a) Z. Li, J. Lu, Y. M. Qin, S. D. Li, S. H. Qin, *J. Mater. Chem. C*, 2013, **1**, 5944; (b) S. D. Li, J. Lu, H. K. Ma, J. Xu, D. P. Yan, M. Wei, D. G. Evans and X. Duan, *Langmuir*, 2011, **27**, 11501.
- B. Valeur. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Berlin, Germany, 2001; Vol. 125.
- (a) M. Glasbeek and H. Zhang, *Chem. Rev.*, 2004, **104**, 1929; (b) S. L. Bondarev, V. N. Knyuksho, V. I. Stepuro, A. P. Stupak, and A. A. Turban, *J Appl. Spectrosc.*, 2004, **71**, 194; (c) C. Chang, Y. Kao and E. W. G. Diau, *Chem. Phys. Lett.*, 2003, **374**, 110.
- C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319. E_T(30) is simply defined as the molar electronic transition energies of dissolved pyridinium N-phenolate betaine dye. The use of directly determined E_T(30) values in correlations with other energy-based solvent-dependent processes has the advantage of giving immediate insight in the magnitude of the solvent effects observed.
- Easter, D. C.; Baronavski, A. P. *Chem. Phys. Lett.* 1993, **201**, 153.

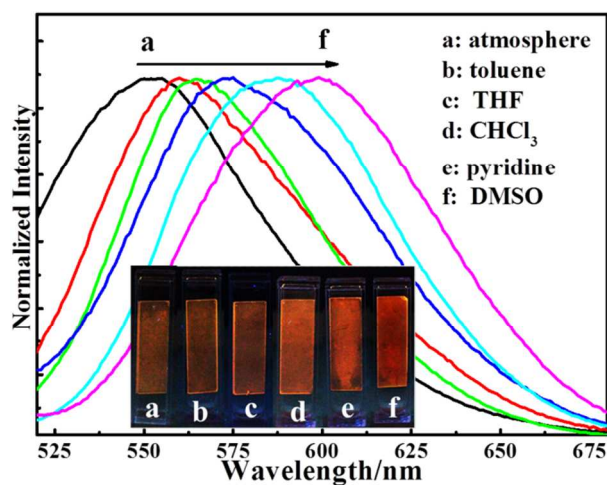
TOC

Luminous Composite Ultrathin Films of DCM Dye Assembled with Layered Double Hydroxides and its fluorescence solvatochromism properties for polarity sensors

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Graphical Abstract



The PS-PAA@DCM/LDH ultrathin films were fabricated by the layer-by-layer assembly method. The composite films exhibited fast and reversible fluorescence solvatochromism towards solvent vapors with the emission color being modulated from 550 to 600 nm.