

Supporting Information for

Reversible pH-modified Fluorescence Transition in the Block Copolymer Micelles Enwrapping with Zinc(II) Fluorescent Complex

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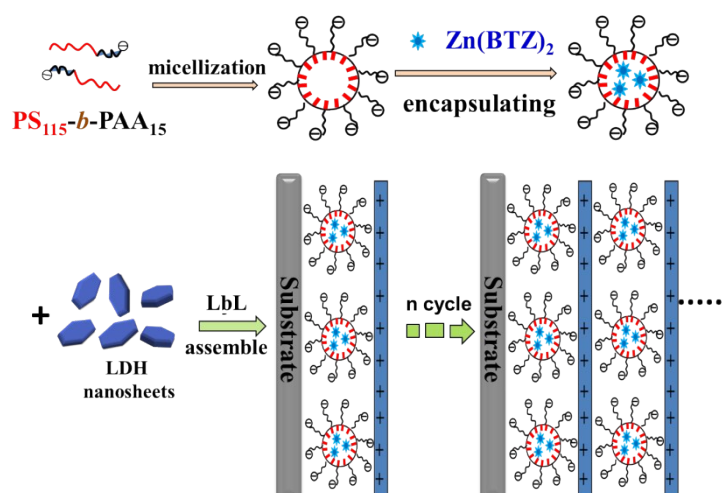
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Scheme S1. Process scheme of formation of $\text{PS-}b\text{-PAA}@$ $\text{Zn}(\text{BTZ})_2$ micelle and fabrication of (micelles/LDH)_{*n*} films.

1. Structure and Morphology Characterization for Micelles and (micelles/LDH)_{*n*} Films

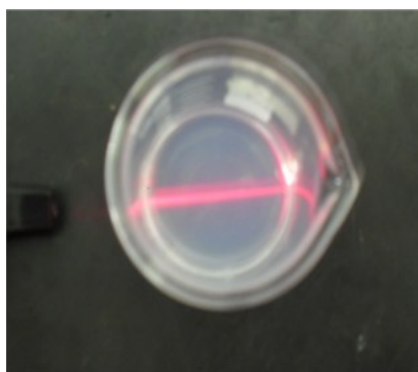


Figure S1. The photograph of $\text{Zn}(\text{BTZ})_2@$ PS-*b*-PAA micelles at pH = 6.0 with Tyndall effect.

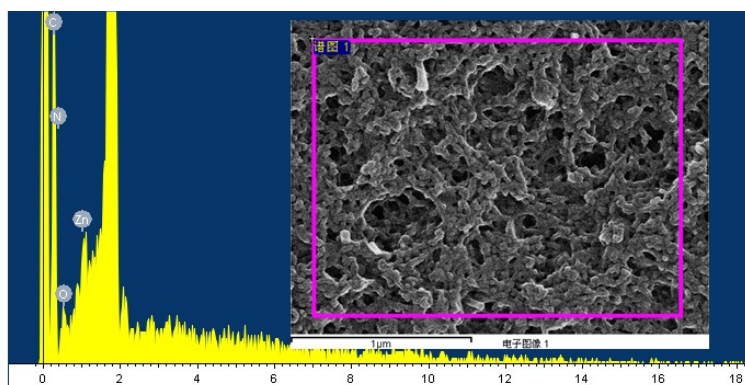


Figure S2. SEM-EDX analysis of $\text{Zn}(\text{BTZ})_2@PS-b\text{-PAA}$ micelles at $\text{pH} = 7.5$.

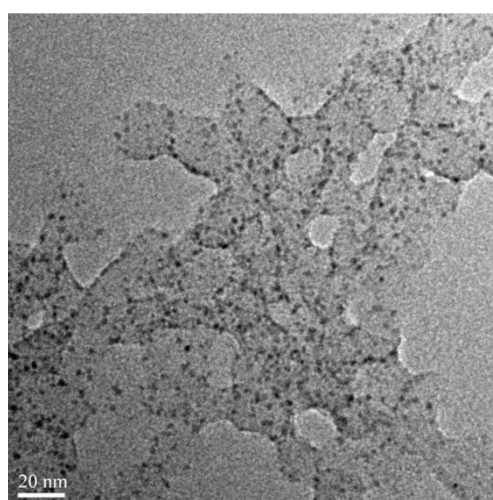


Figure S3. TEM image of $\text{Zn}(\text{BTZ})_2@PS-b\text{-PAA}$ micelles at $\text{pH} = 7.5$.

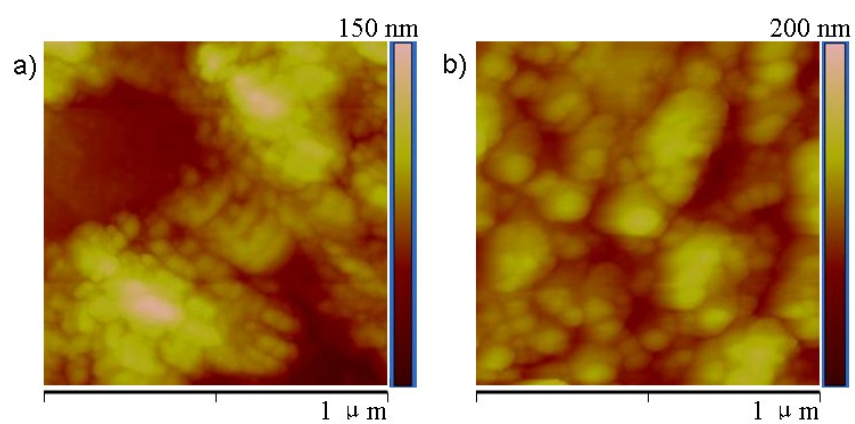


Figure S4. Tapping-mode AFM topographical 2D images of $\text{Zn}(\text{BTZ})_2@PS-b\text{-PAA}$ micelles: a) $\text{pH} = 7.5$ and b) $\text{pH} = 9.0$.

Atomic force microscope (AFM) images display that the individual micelle is spherical morphology and around 35 and 60 nm in diameter for pH = 7.5 and 9.0, respectively.

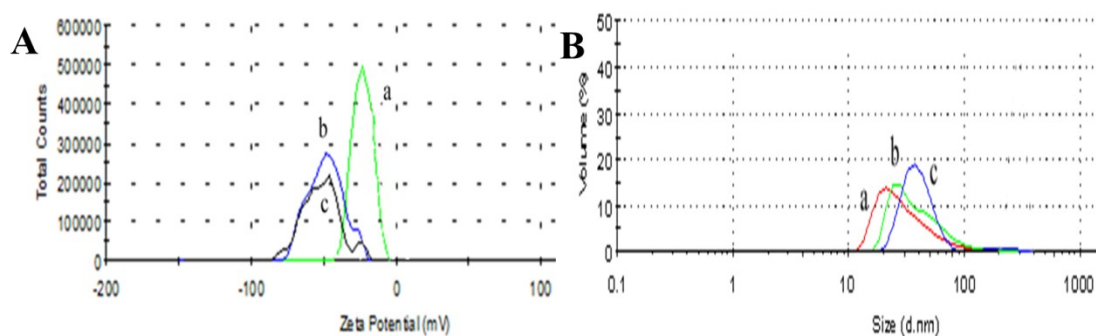


Figure S5. Zeta-potential and dynamic lighting scattering (DLS) diameter as a function of pH value of $\text{Zn}(\text{BTZ})_2@PS\text{-}b\text{-PAA}$ micelle: a, b, c) pH = 6.0, 7.5, 9.0, respectively.

2. pH-induced Photophysical Properties of $\text{Zn}(\text{BTZ})_2@PS\text{-}b\text{-PAA}$ Micelles and (micelles/LDH)_n Films

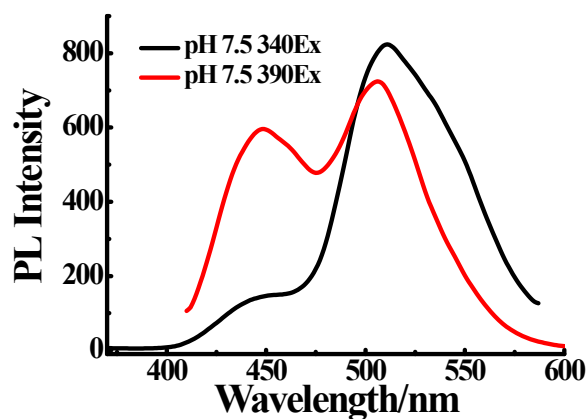


Figure S6. PL emission spectra of $\text{Zn}(\text{BTZ})_2@PS\text{-}b\text{-PAA}$ micelles at pH = 7.5 under 340 and 390 nm excitation.

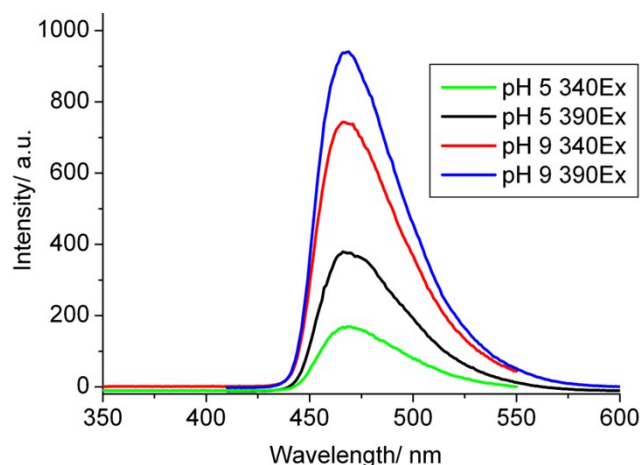


Figure S7. PL emission spectra of Zn(BTZ)₂ DMF solution at pH = 5.0 and 9.0 under 340 and 390 nm excitation, respectively.

Table S1. The single or double-exponential fitting of fluorescence decay data of Zn(BTZ)₂ solution, micelles and films under pH = 6.0, 9.0 at 375 nm laser excitation.

Samples	τ_i (ns) ^[a]	A_i (%)	$\langle\tau\rangle$ (ns)	χ^2 ^[b]
Zn(BTZ) ₂ DMF solution at 460 nm	4.53	100	4.53	1.29
Zn(BTZ) ₂ @PS- <i>b</i> -PAA micelles at 460 nm for pH = 9.0	4.06	100	4.06	1.21
(Zn(BTZ) ₂ @PS- <i>b</i> -PAA/LDH) ₁₆ at 460 nm for pH = 9.0	2.06	57.94	3.36	1.09
	5.16	42.06		
Zn(BTZ) ₂ @PS- <i>b</i> -PAA micelles at 510 nm for pH = 6.0	0.69	15.59	3.73	1.20
	4.29	84.41		
(Zn(BTZ) ₂ @PS- <i>b</i> -PAA/LDH) ₁₆ at 510 nm after HCl treatment	1.79	51.24	2.95	1.10
	4.16	48.76		

[a] τ_i ($i = 1, 2$) is the fitted fluorescence lifetime. A_i is the percentage of τ_i . In the biexponential case, $\langle\tau\rangle = A_1\tau_1 + A_2\tau_2$; $A_1 + A_2 = 1$.

[b] the goodness of fit is indicated by the value of χ^2 .

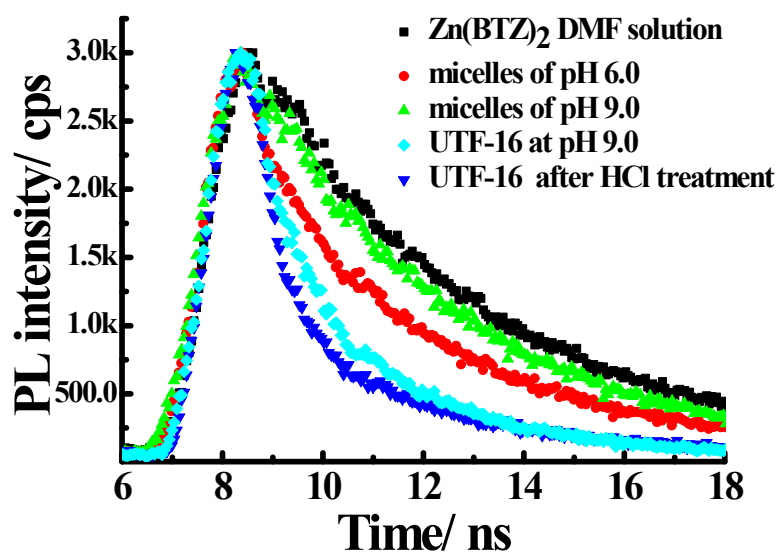


Figure S8. Fluorescence decay profile for Zn(BTZ)₂ DMF solution, Zn(BTZ)₂@PS-*b*-PAA micelles at pH 6.0 and 9.0, (Zn(BTZ)₂@PS-*b*-PAA/LDH)₁₆ film at pH 9.0 and the film exposed to HCl atmosphere for 2 mins.

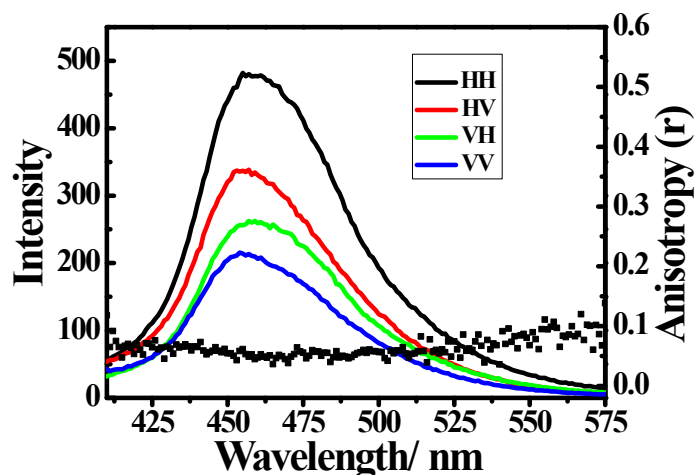


Figure S9. Polarized fluorescence profiles in the HH, HV, VV, VH modes and anisotropic value (r) for Zn(BTZ)₂ DMF solution under 390nm excitation.

The anisotropic value $r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH})$, where $G = I_{HV} / I_{HH}$. I_{VH} donates the PL intensity obtained with vertical polarized excitation and horizontal polarized detection, and I_{VV} , I_{HH} , I_{HV} are defined similarly.

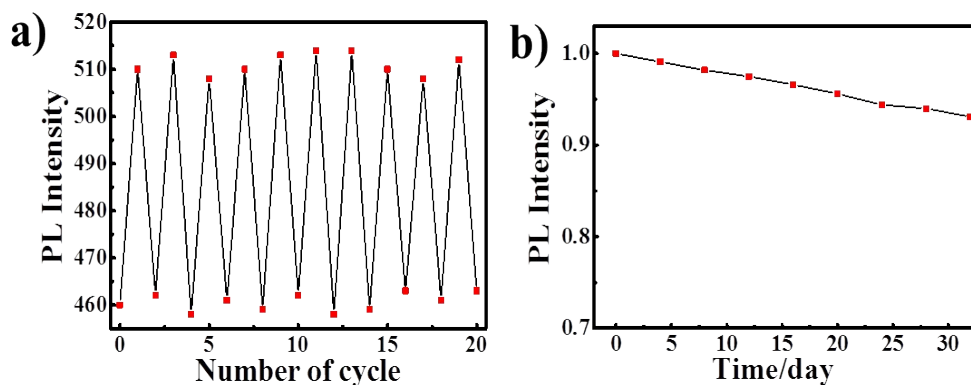


Figure S10. (a) Reversibility transition from green to blue emission of Zn(BTZ)₂@PS-*b*-PAA micelles repeated for 20 times; (b) the PL intensity of Zn(BTZ)₂@PS-*b*-PAA micelles (stored at room temperature) recorded for 32 days.

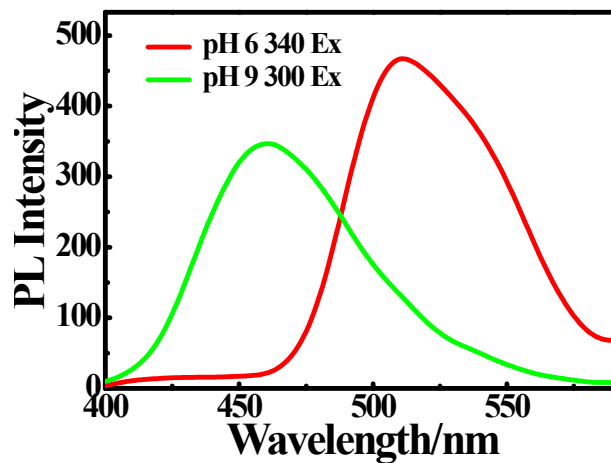


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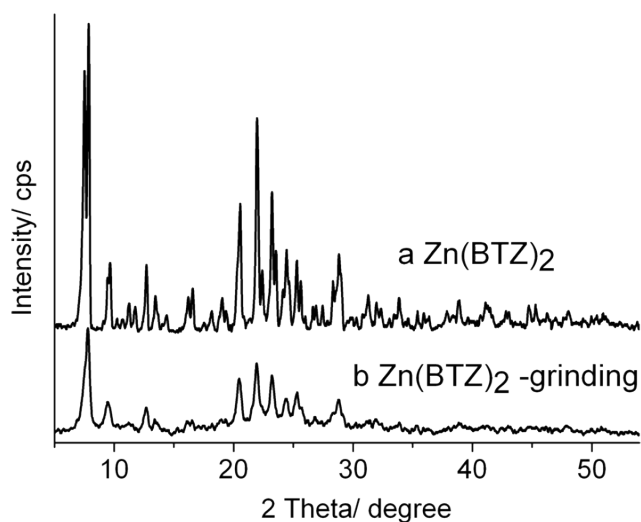


Figure S12. Power X-ray diffraction patterns of Zn(BTZ)₂ molecules and after grinding.

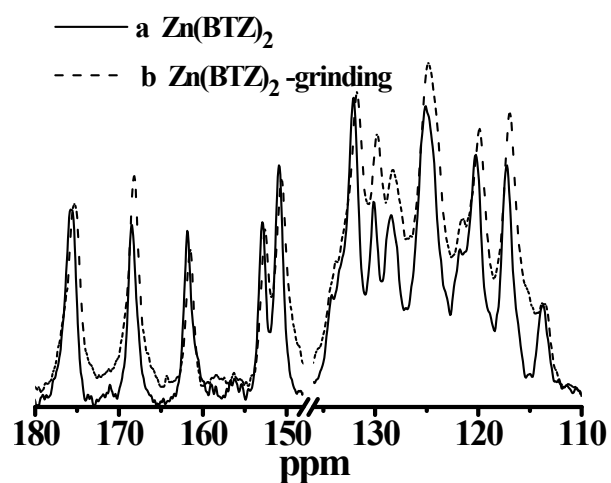


Figure S13. CPTOSS ¹³C NMR spectra of Zn(BTZ)₂ molecules and after grinding.

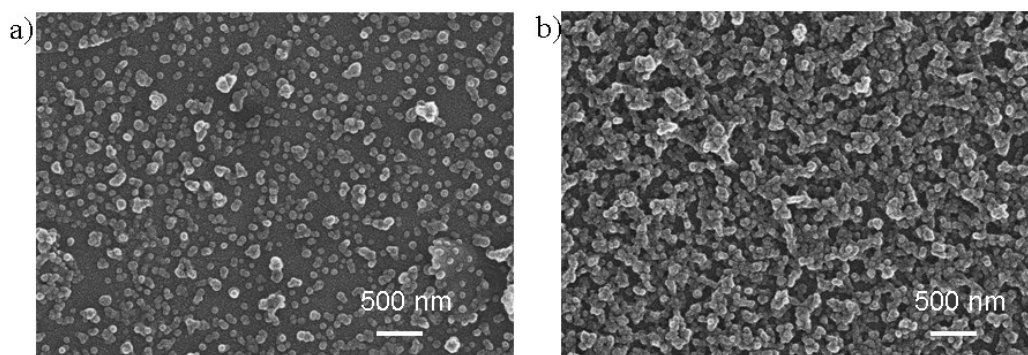


Figure S14. SEM top view images of (micelles/LDH)_n film with a) $n = 4$ and b) $n = 12$.

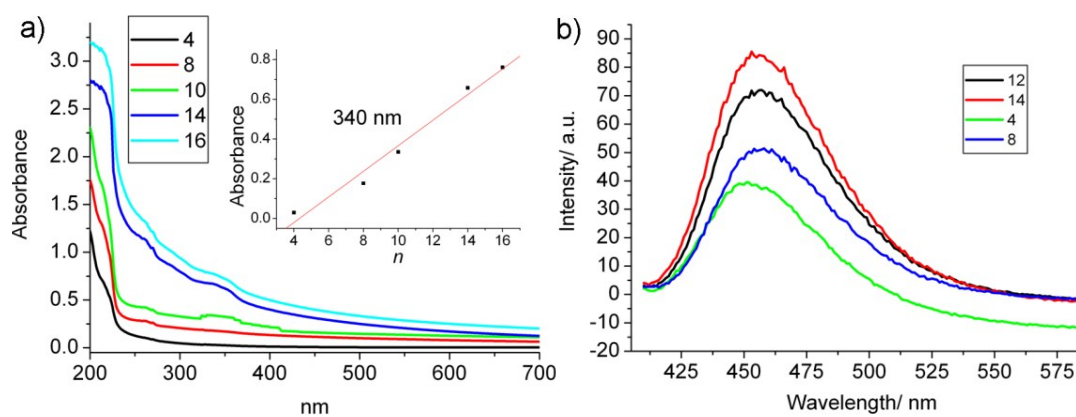


Figure S15. a) Absorption spectra of (micelles/PDDA)_n films. The inset plots show the absorbance at 340 nm vs. the number of bilayers n . b) PL emission spectra of (micelles/PDDA)_n films with variable bilayers under 390 nm excitation.