

Electronic Supplementary Information

Multivalent Supramolecular Assembly with Ultralong Organic Room Temperature Phosphorescence, High Transfer Efficiency and Ultrahigh Antenna Effect in Water

Wei-Lei Zhou^{a,b}, Wenjing Lin^a, Yong Chen^a, Xian-Yin Dai^a, Zhixue Liu^a and Yu Liu^{a*}

^aDepartment of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University

^bCollege of Chemistry and Materials Science, Inner Mongolia Key Laboratory of Chemistry for Nature Products and Synthesis for Functional Molecules, Inner Mongolia Minzu University, Tongliao 028000, People's Republic of China

Table of Contents

Fig. S1. Zeta potential results of (a) HABr, (b) HABr/CB[8], (c) LP and (d) HABr/CB[8]/LP ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [LP] = 0.02 wt %, 298 K).

Fig. S2. Phosphorescence spectra of (a) HABr/CB[8] and HABr/CB[8]/SP/LP(sodium polyacrylate = SP); (b) HABr/CB[8] and HABr/CB[8]/SA/LP(sodium alginate = SA) in water ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [LP] = 0.02 wt %, [SP] = 0.02 wt %, [SA] = 0.02 wt %, λ_{ex} = 300 nm).

Fig. S3. Phosphorescence lifetime decay fitting curves of (a) HABr/CB[8] and (b) HABr/CB[8]/LP at 500 nm at 298 K.

Fig. S4. The quantum yield of (a) HABr/CB[8] and (b) HABr/CB[8]/LP in aqueous solution

Fig. S5. SEM image of (a) HABr/CB[8], (b) HABr/CB[8]/LP and TEM image of (c) HABr/CB[8], (d) HABr/CB[8]/LP.

Fig. S6. Phosphorescence lifetime decay fitting curve of (a) HABr/CB[8]/LP/RhB measured for 500 nm at 298 K and (b) HABr/CB[8]/LP/SR101 measured for 500 nm at 298 K.

Fig. S7. Fluorescence lifetime decay fitting curve of (a) RhB, (b) SR101. Phosphorescence lifetime decay fitting curve of (c) HABr/CB[8]/LP/RhB measured for 585 nm at 298 K, (d) HABr/CB[8]/LP/SR101 measured for 612 nm at 298 K.

Fig. S8. Phosphorescence spectra of (a) HABr/CB[8]/LP and HABr/CB[8]/LP/RhB; (c) HABr/CB[8]/LP and HABr/CB[8]/LP/SR101 in water (λ_{ex} = 300 nm). The normalized phosphorescence spectra of (b) HABr/CB[8]/LP (red line, λ_{ex} = 300 nm), HABr/CB[8]/LP/RhB (blue line, λ_{ex} = 300 nm), HABr/CB[8]/LP/RhB (black line, λ_{ex} = 550 nm) and (d) HABr/CB[8]/LP (red line, λ_{ex} = 300 nm), HABr/CB[8]/LP/SR101 (blue line, λ_{ex} = 300 nm), HABr/CB[8]/LP/SR101 (black line, λ_{ex} = 580 nm) in water.

Table S1. Energy transfer efficiency (Φ_{ET}) and antenna effect of RTP reported in the literature.

Fig. S9. (a) Phosphorescence spectrum (delayed 0.2 ms) of HABr/CB[8] in aqueous solution with different concentrations of SR101. Phosphorescence spectra of (b) HABr/CB[8] and HABr/CB[8]/SR101. The normalized phosphorescence spectra of (c) HABr/CB[8] (red line, $\lambda_{ex} = 300$ nm), HABr/CB[8]/SR101 (red line, $\lambda_{ex} = 300$ nm), HABr/CB[8]/SR101 (black line, $\lambda_{ex} = 580$ nm). (d) Phosphorescence spectrum (delayed 0.2 ms) of RhB and SR101 in aqueous solution.

Fig. S10. (a) Phosphorescence spectrum (delayed 0.2 ms) and (b) Antenna effect/ Φ_{ET} of HABr/CB[8] in aqueous solution with different concentrations of RhB. Phosphorescence spectra of (c) HABr/CB[8] and HABr/CB[8]/RhB. The normalized phosphorescence spectra of (b) HABr/CB[8] (red line, $\lambda_{ex} = 300$ nm), HABr/CB[8]/RhB (red line, $\lambda_{ex} = 300$ nm), HABr/CB[8]/RhB (black line, $\lambda_{ex} = 550$ nm).

Fig. S11. The photographs writing “102” with HABr/CB[8]/0.005SR101 on the filter paper under UV light.

Fig. S12. Phosphorescence spectra of HABr/CB[8]/LP at different delay times for 0.2 ms, 0.6 ms, 1.0 ms, 1.4 ms, 2.2 ms, 4.2 ms, respectively in water at 298 K (Ex. Slit = 5 nm, Em. Slit = 10 nm, [HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [LP] = 0.02 wt %, $\lambda_{ex} = 300$ nm).

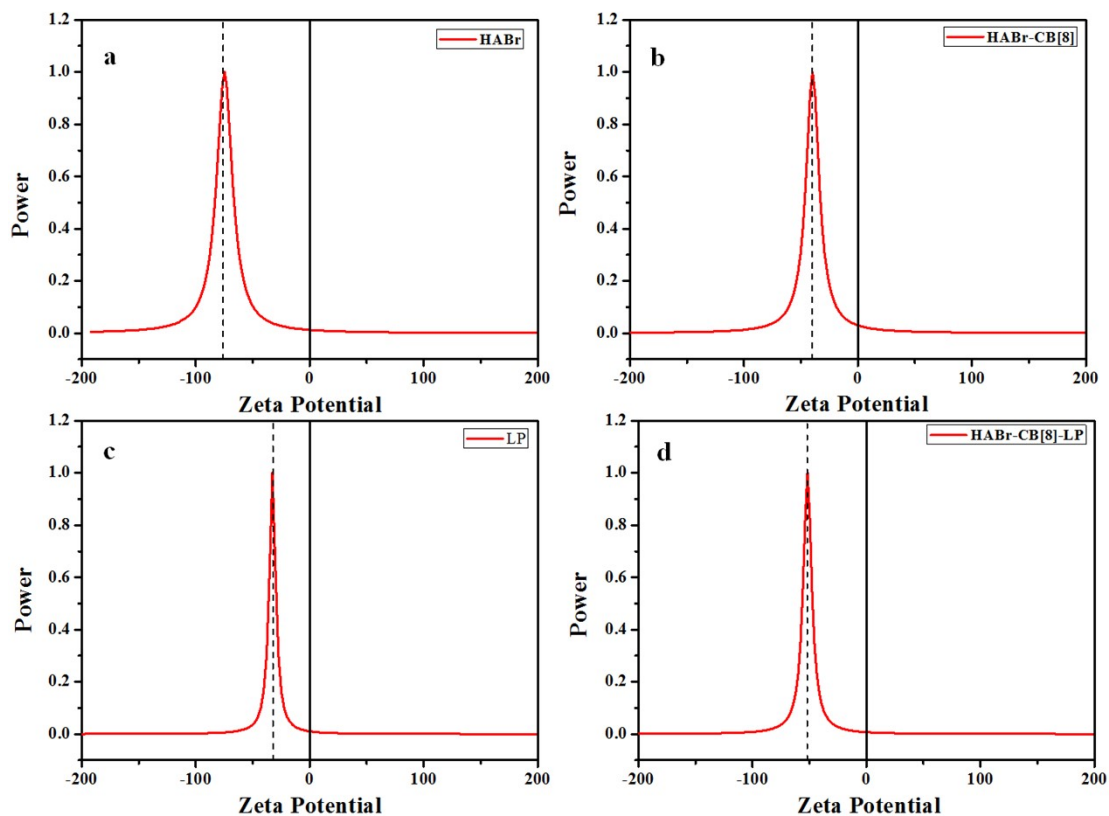


Fig. S1 Zeta potential results of (a) HABr, (b) HABr/CB[8], (c) LP and (d) HABr/CB[8]/LP ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [LP] = 0.02 wt %, 298 K).

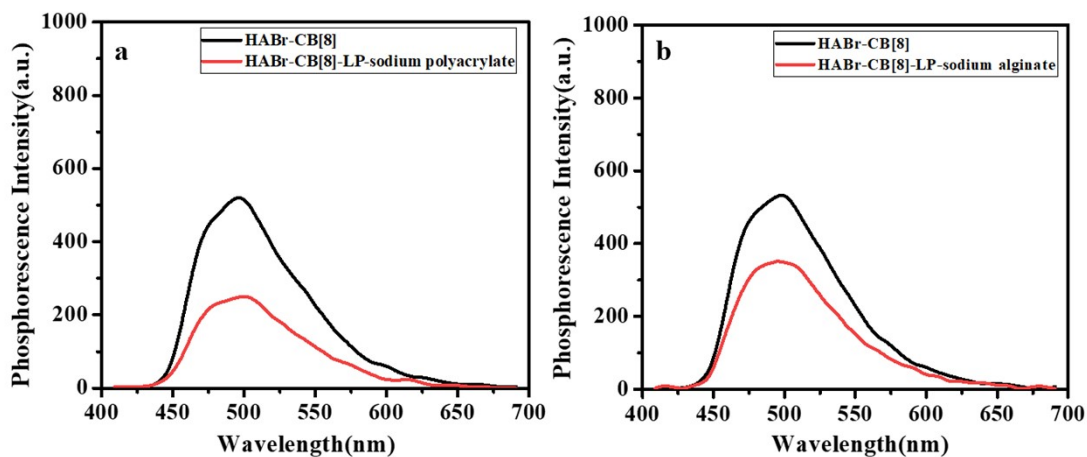
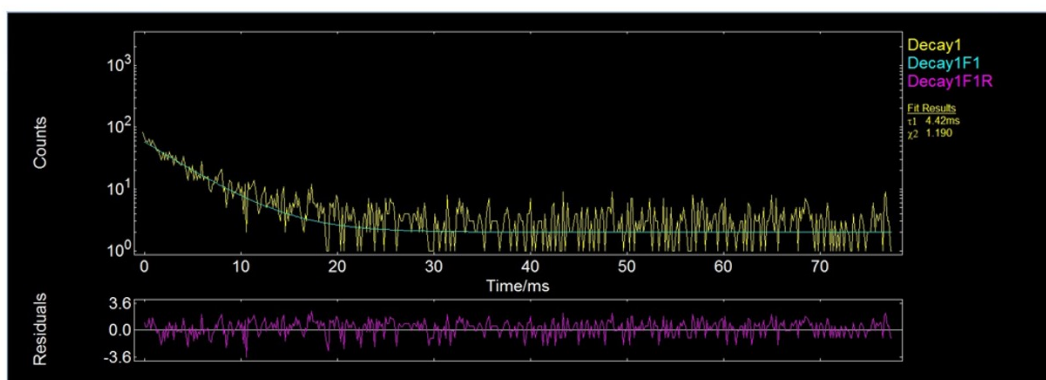


Fig. S2 Phosphorescence spectra of (a) HABr/CB[8] and HABr/CB[8]/SP/LP(sodium polyacrylate = SP); (b) HABr/CB[8] and HABr/CB[8]/SA/LP(sodium alginate = SA) in water ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [LP] = 0.02 wt %, [SP] = 0.02 wt %, [SA] = 0.02 wt %, λ_{ex} = 300 nm).

a



b

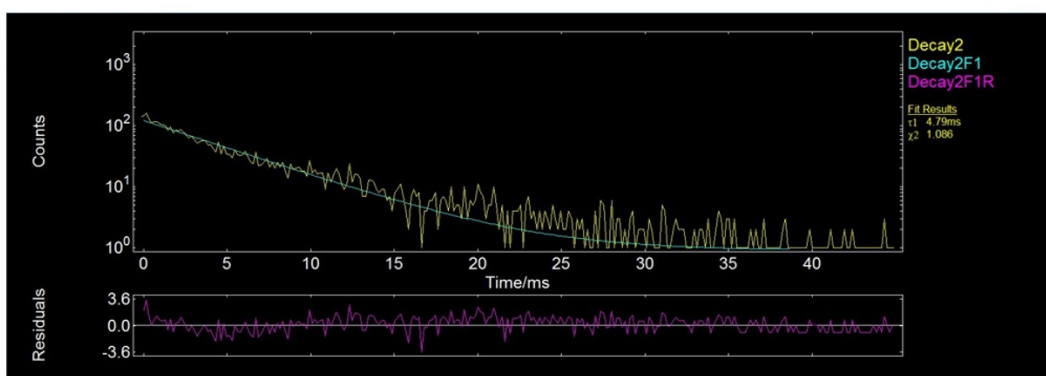
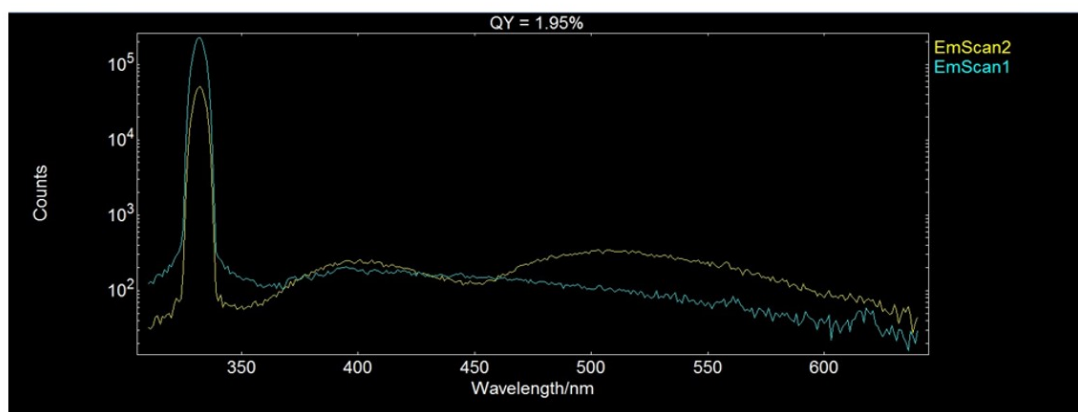


Fig. S3 Phosphorescence lifetime decay fitting curves of (a) HABr/CB[8] and (b) HABr/CB[8]/LP at 500 nm at 298 K ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, LP = 0.02 wt %).

a



b

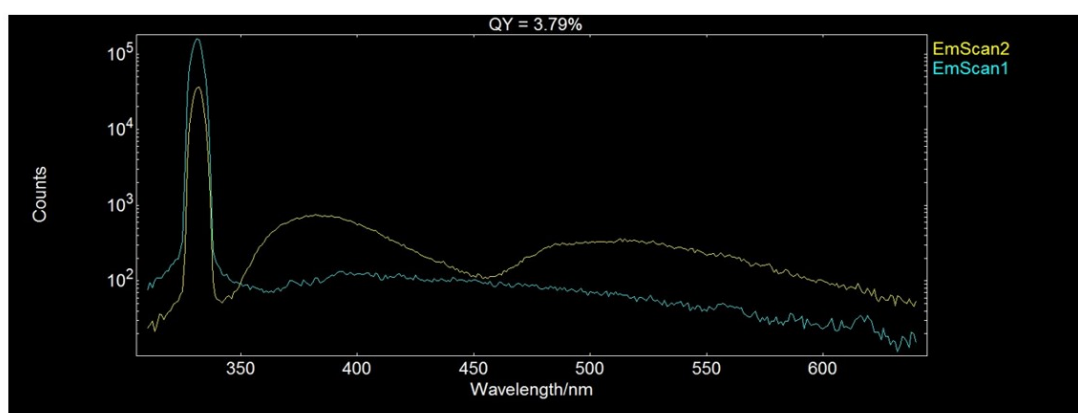


Fig. S4 The quantum yield of (a) HABr/CB[8] and (b) HABr/CB[8]/LP in aqueous solution ($[HABr] = 0.1 \text{ mM}$, $[CB[8]] = 0.05 \text{ mM}$, LP = 0.02 wt %).

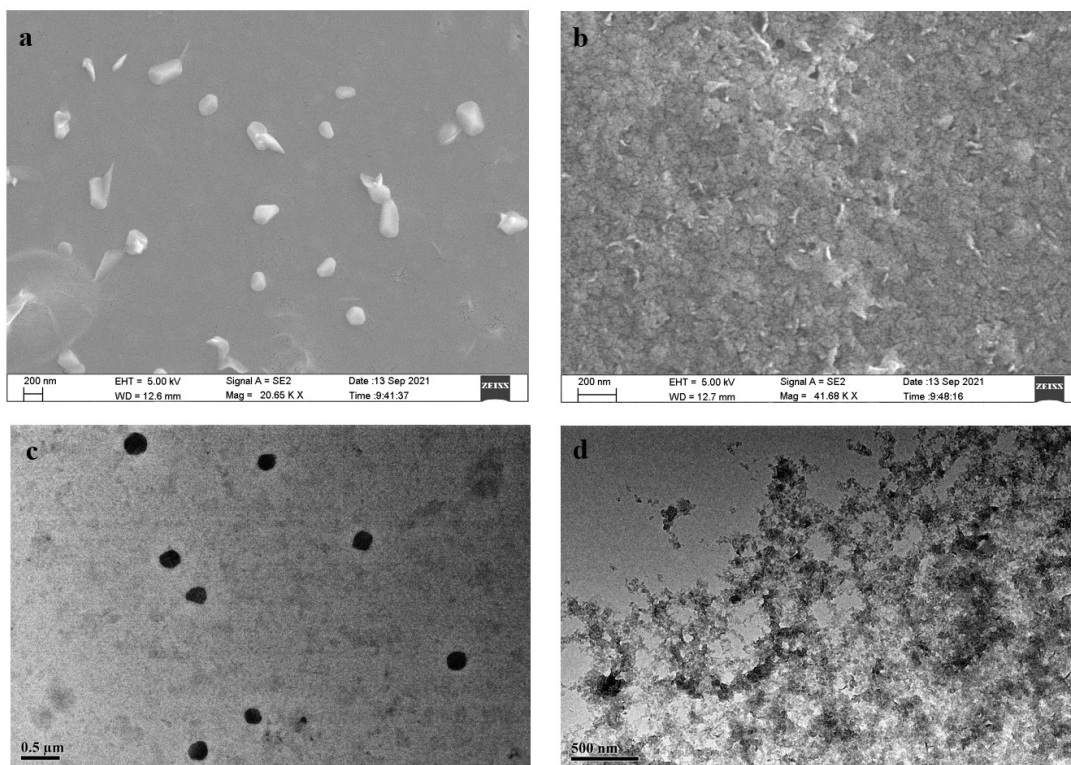


Fig. S5 SEM image of (a) HABr/CB[8], (b) HABr/CB[8]/LP and TEM image of (c) HABr/CB[8], (d) HABr/CB[8]/LP.

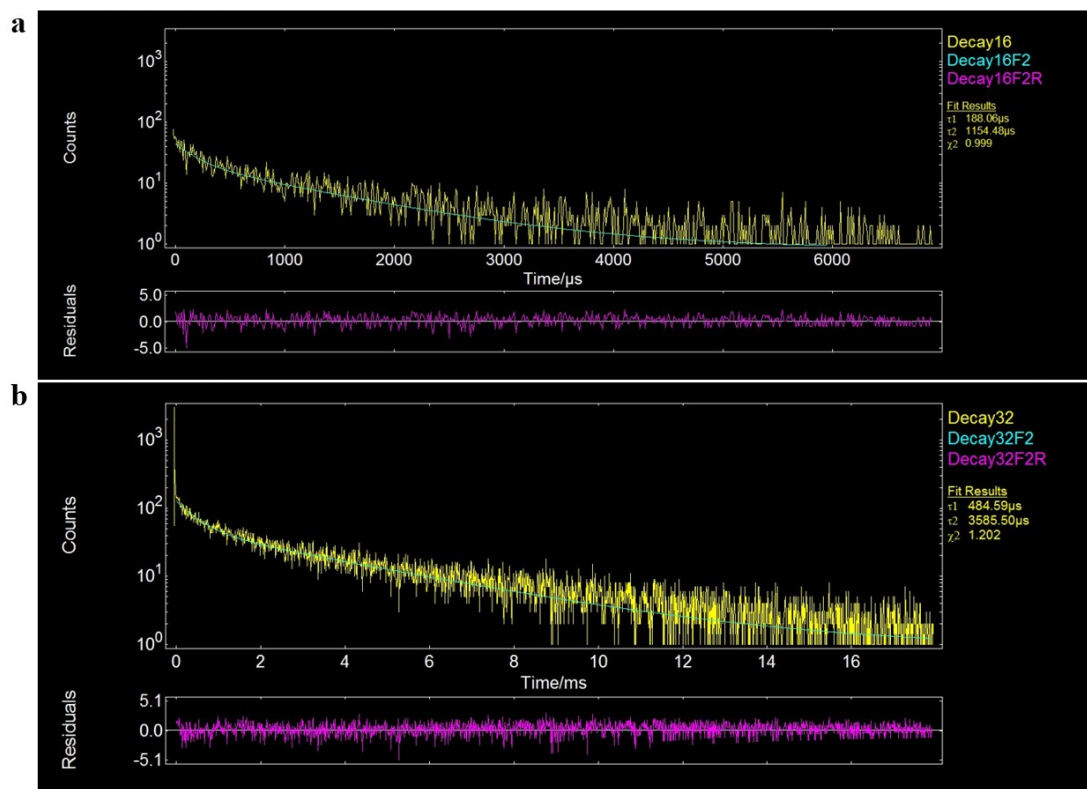


Fig. S6 Phosphorescence lifetime decay fitting curve of (a) HABr/CB[8]/LP/RhB measured for 500 nm at 298 K and (b) HABr/CB[8]/LP/SR101 measured for 500 nm at 298 K. ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, LP = 0.02 wt %, [RhB] = 4.0×10^{-6} M, [SR101] = 1.3×10^{-6} M).

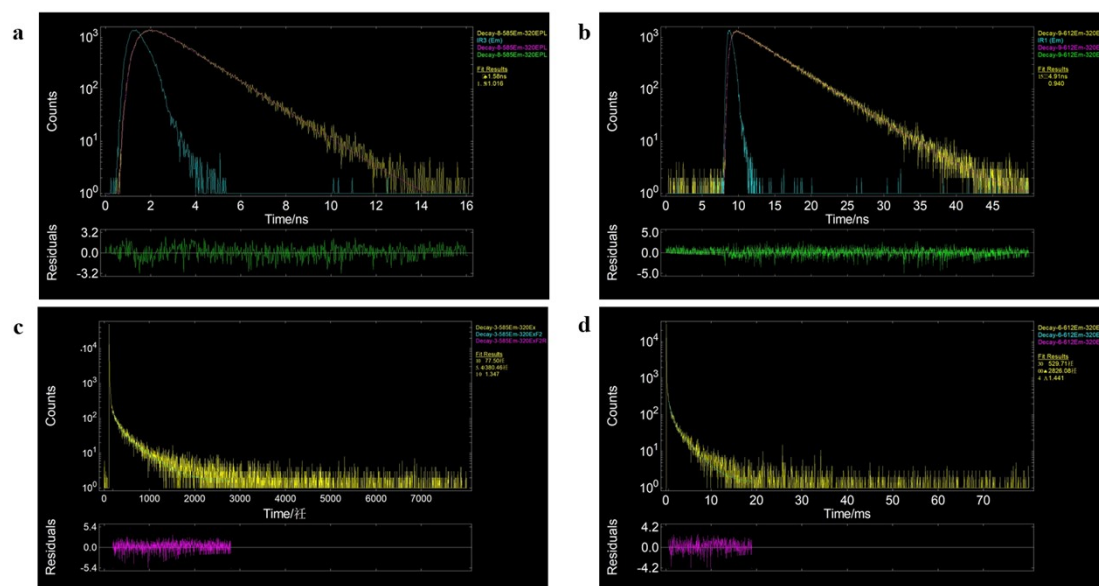


Fig. S7 Fluorescence lifetime decay fitting curve of (a) RhB, (b) SR101. Phosphorescence lifetime decay fitting curve of (c) HABr/CB[8]/LP/RhB measured for 585 nm at 298 K, (d) HABr/CB[8]/LP/SR101 measured for 612 nm at 298 K. ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, LP = 0.02 wt %, [RhB] = 4.0×10^{-6} M, [SR101] = 1.3×10^{-6} M).

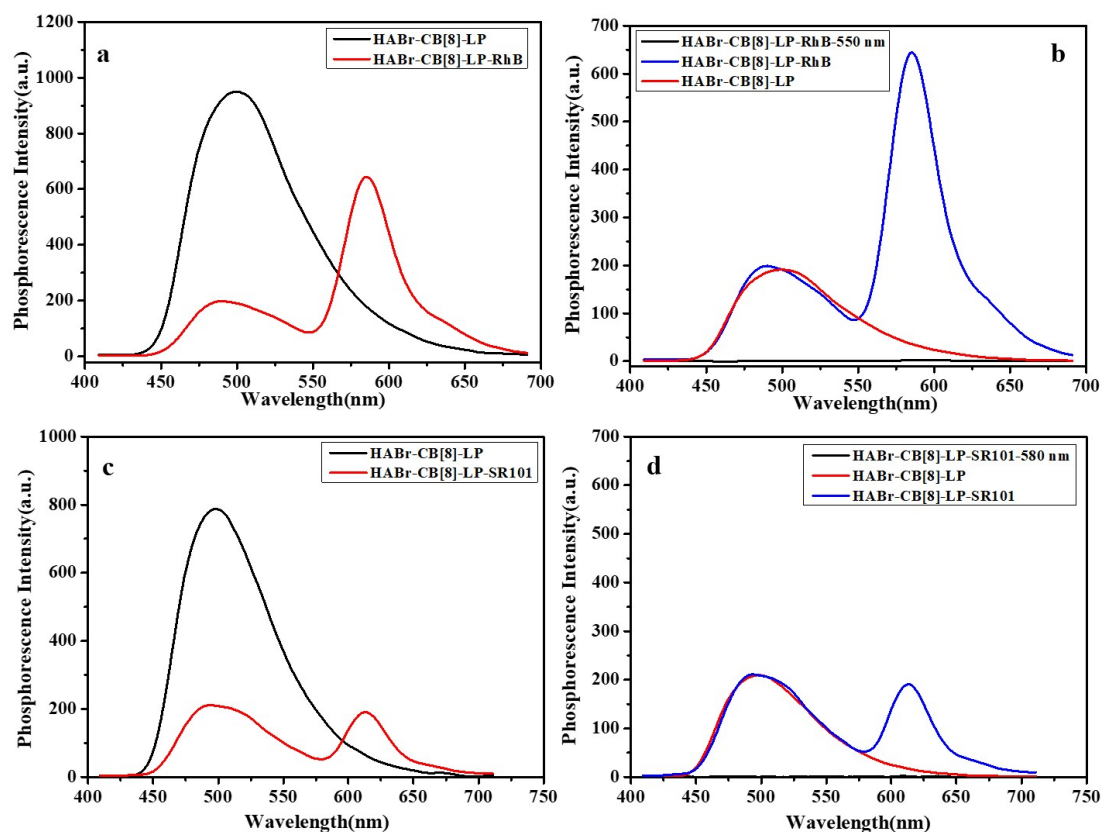


Fig. S8 Phosphorescence spectra of (a) HABr/CB[8]/LP and HABr/CB[8]/LP/RhB; (c) HABr/CB[8]/LP and HABr/CB[8]/LP/SR101 in water ($\lambda_{\text{ex}} = 300$ nm). The normalized phosphorescence spectra of (b) HABr/CB[8]/LP (red line, $\lambda_{\text{ex}} = 300$ nm), HABr/CB[8]/LP/RhB (blue line, $\lambda_{\text{ex}} = 300$ nm), HABr/CB[8]/LP/RhB (black line, $\lambda_{\text{ex}} = 550$ nm) and (d) HABr/CB[8]/LP (red line, $\lambda_{\text{ex}} = 300$ nm), HABr/CB[8]/LP/SR101 (blue line, $\lambda_{\text{ex}} = 300$ nm), HABr/CB[8]/LP/SR101 (black line, $\lambda_{\text{ex}} = 580$ nm) in water. ($[\text{HABr}] = 0.1$ mM, $[\text{CB}[8]] = 0.05$ mM, LP = 0.02 wt %, $[\text{RhB}] = 4.0 \times 10^{-6}$ M, $[\text{SR101}] = 1.3 \times 10^{-6}$ M).

Table S1. Energy transfer efficiency (Φ_{ET}) and antenna effect of RTP reported in the literature.

name	Φ_{ET}	morphology	τ (dye)	literature
	Antenna Effect			
(IPA@EosinY)/LDH	99.7%, -	Solid	0.95 ms	Ref.23
BTA-ME-1	81.13%, -	co-crystals	1.0 ms	Ref.24
BTA-ME-2	78.97%, -		0.7 ms	
CD-PY@CB[8]@RhB	84%, 36.42%	water	0.28 ms	Ref.15
SR101-doped CS-PVA	81%, -	Solid films	490 ms	Ref.21a
SRG-doped CS-PVA	70%, -	Solid films	750 ms	
CPthBr-LP/SRG	32%, -	water	163.5 μ s	Ref.19
CPthBr-LP/SR101	60%, -		60.4 μ s	
HABr/CB[8]/LP/RhB	80.0%, 361.6	water	0.31 ms	This work
HABr/CB[8]/LP/SR101	73.4%, 307.5		2.10 ms	

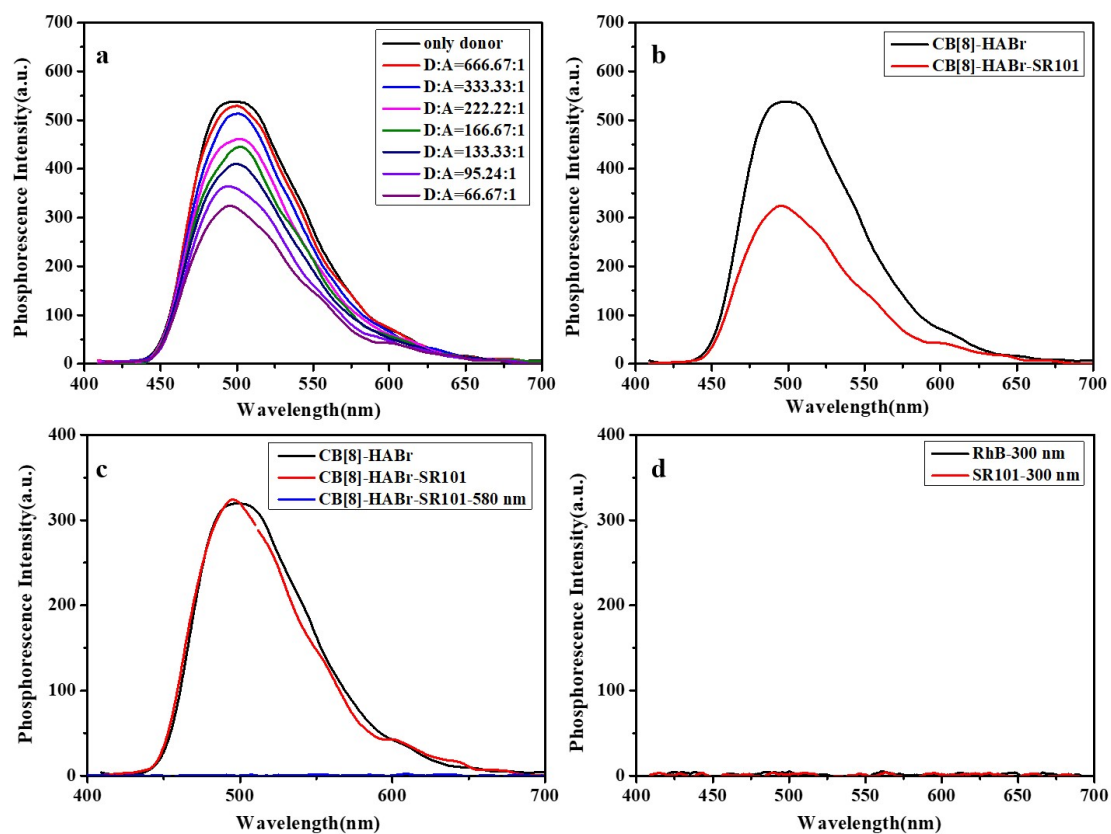


Fig. S9 (a) Phosphorescence spectrum (delayed 0.2 ms) of HABr/CB[8] in aqueous solution with different concentrations of SR101. Phosphorescence spectra of (b) HABr/CB[8] and HABr/CB[8]/SR101. The normalized phosphorescence spectra of (c) HABr/CB[8] (red line, $\lambda_{\text{ex}} = 300$ nm), HABr/CB[8]/SR101 (red line, $\lambda_{\text{ex}} = 300$ nm), HABr/CB[8]/SR101 (black line, $\lambda_{\text{ex}} = 580$ nm). (d) Phosphorescence spectrum (delayed 0.2 ms) of RhB and SR101 in aqueous solution. ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [SR101] = 1.3×10^{-6} M, $\lambda_{\text{ex}} = 300$ nm, 298 K).

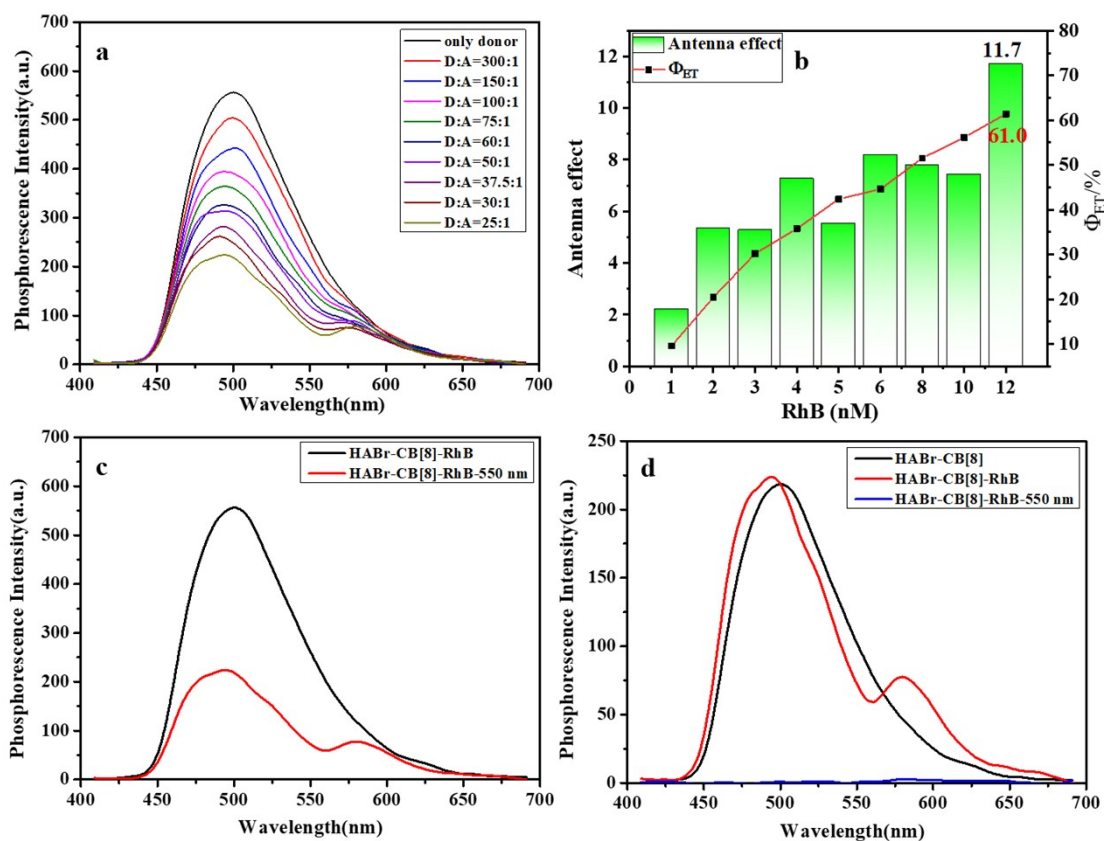


Fig. S10 (a) Phosphorescence spectrum (delayed 0.2 ms) and (b) Antenna effect/ Φ_{ET} of HABr/CB[8] in aqueous solution with different concentrations of RhB. Phosphorescence spectra of (c) HABr/CB[8] and HABr/CB[8]/RhB. The normalized phosphorescence spectra of (d) HABr/CB[8] (red line, $\lambda_{ex} = 300$ nm), HABr/CB[8]/RhB (red line, $\lambda_{ex} = 300$ nm), HABr/CB[8]/RhB (black line, $\lambda_{ex} = 550$ nm). ([HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [RhB] = 4.0×10^{-6} M, $\lambda_{ex} = 300$ nm, 298 K).



Fig. S11 The photographs writing "102" with HABr/CB[8]/0.005SR101 on the filter paper under UV light.

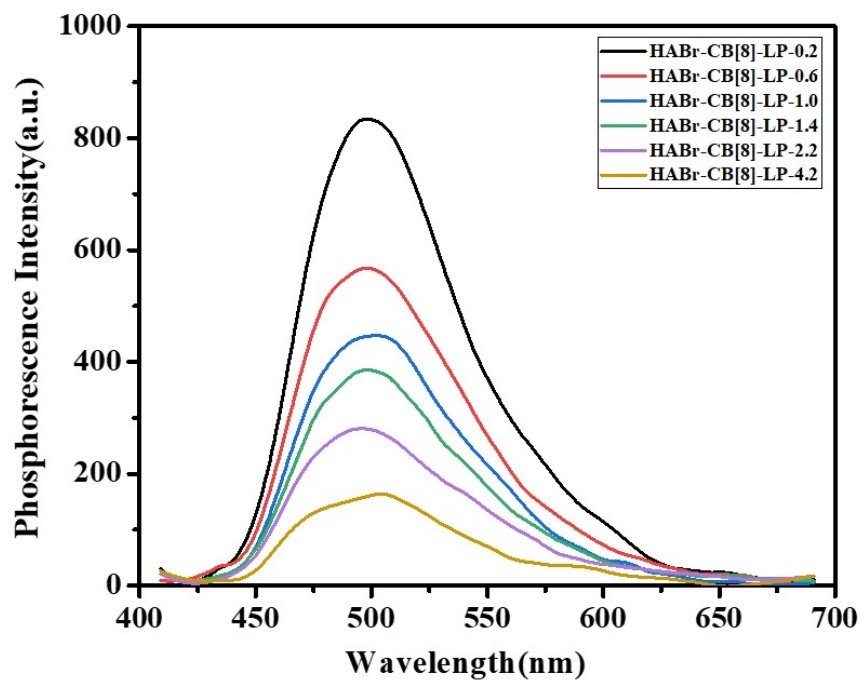


Fig. S12 Phosphorescence spectra of HABr/CB[8]/LP at different delay times for 0.2 ms, 0.6 ms, 1.0 ms, 1.4 ms, 2.2 ms, 4.2 ms, respectively in water at 298 K (Ex. Slit = 5 nm, Em. Slit = 10 nm, [HABr] = 0.1 mM, [CB[8]] = 0.05 mM, [LP] = 0.02 wt %, λ_{ex} = 300 nm).