

Supplementary Information for:

**Confinement of all inorganic perovskite quantum dots assembled in
metal-organic framework for ultrafast scintillator application**

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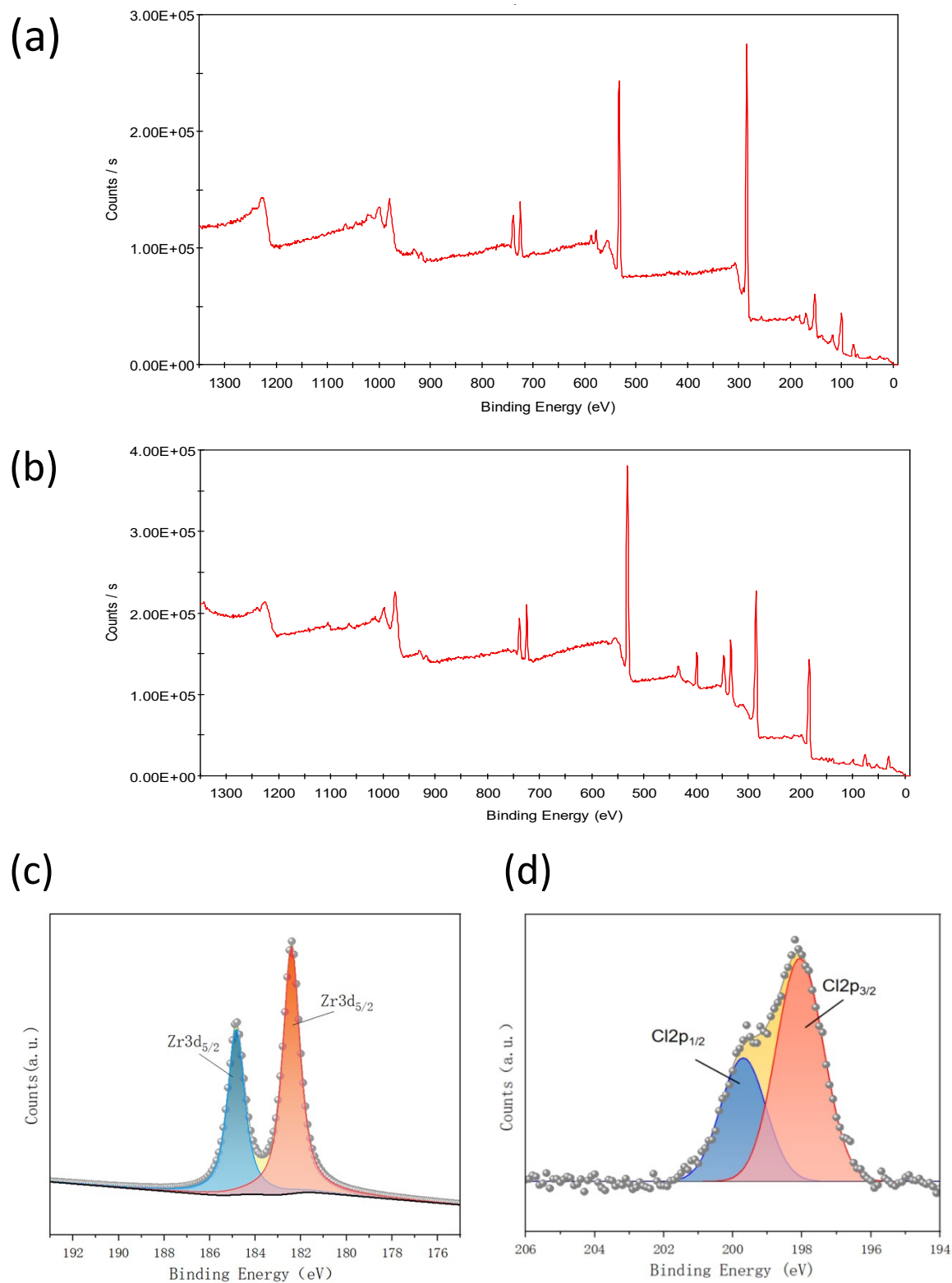
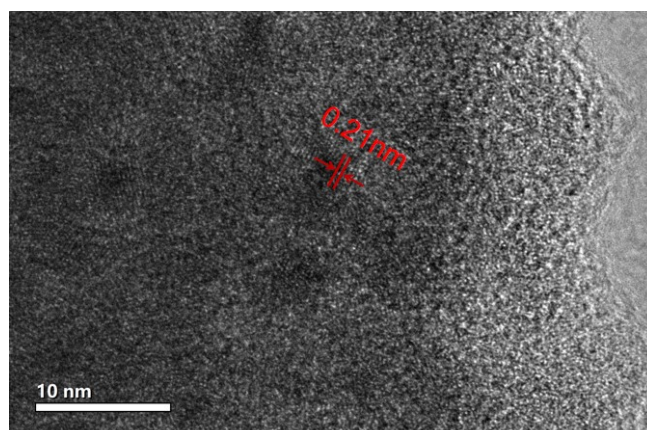
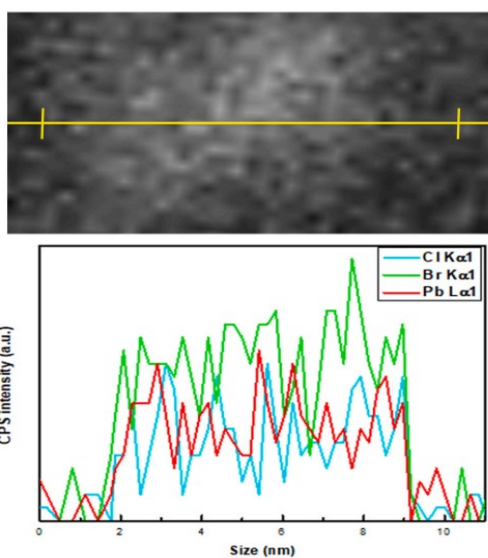


Figure S1 (a) CsPbCl₂Br@MIL-101(Cr) XPS full spectrum scan results (b) CsPbCl₂Br@UiO-67-bpy XPS full spectrum scan results (c) XPS scanning spectrum of Zr (d) XPS scanning spectrum of Cl.

(a)



(b)



(c)

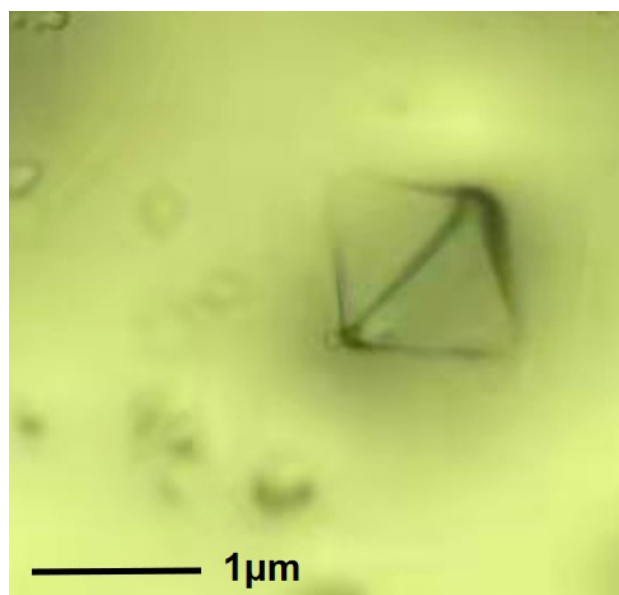


Figure S2 (a) TEM observations CsPbCl₂Br@UiO-67-bpy see perovskite quantum dot lattice fringes; (b) A line scan was performed on suspected quantum dots to determine elements; (c) Metallographic microscopic image of single MIL-101 (Cr) grain.

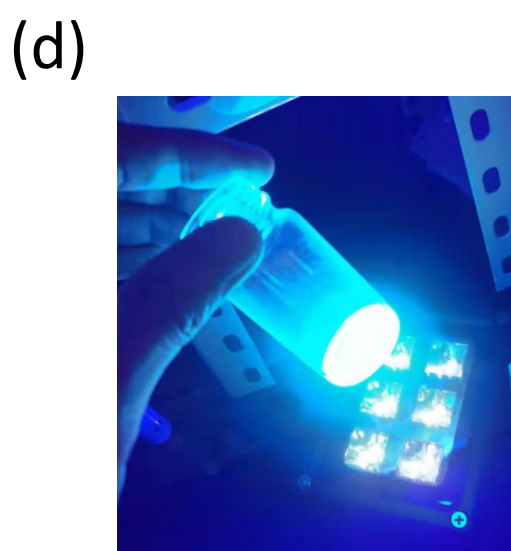
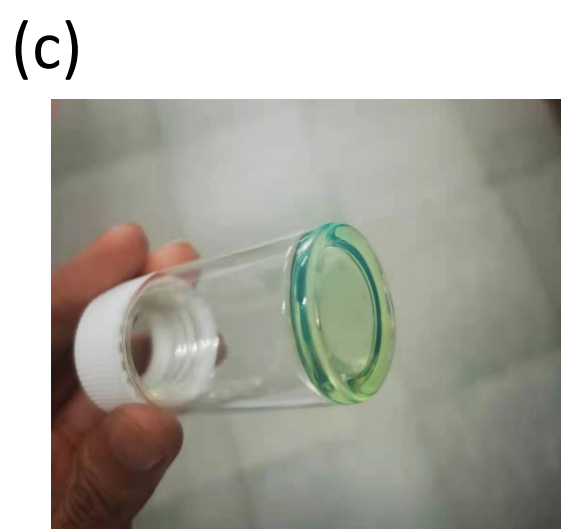
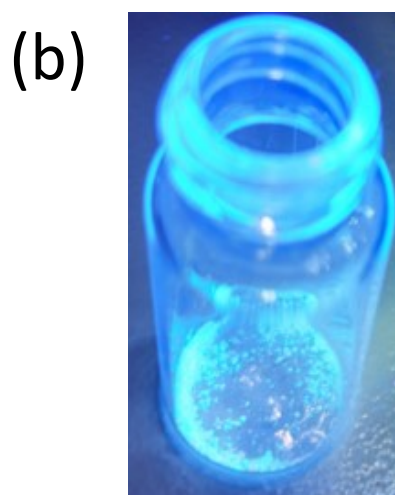
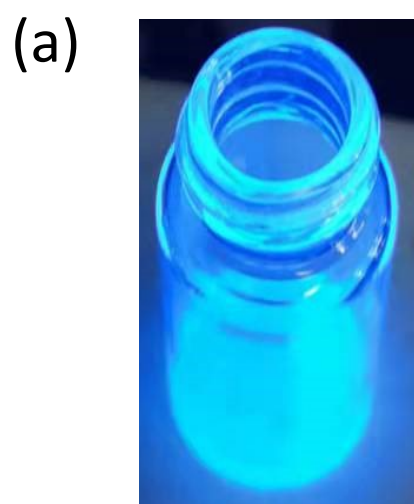


Figure S3 (a) $\text{CsPbCl}_2\text{Br@MIL-101}(\text{Cr})$ dissolved in toluene emits blue light under 365 nm excitation; (b) $\text{CsPbCl}_2\text{Br@MIL-101}(\text{Cr})$ powder emits blue light under 365 nm excitation; (c) scintillation composite after curing; (d) The solidified scintillation composite emits blue light under excitation of 365 nm.

Table S1 Previous research in this field

QDs	Constraint materials/MOF	Application	Year	Reference
ABX ₃	Oleamine, oleic acid	display fields	2016	[1]
CsPbX ₃	SiOx	scintillant	2018	[2]
CH ₃ NH ₃ PbBr ₃	MOF-5	metal ion detection	2018	[3]
CH ₃ NH ₃ PbBr ₃	EuBTC	anti-counterfeiting	2018	[4]
CsPbX ₃	MIL-101 (Cr)	Tunable emission	2019	[5]
MAPbI ₃	UiO-66	Solar cell	2019	[6]
CsPbX ₃	UiO-67	LED	2019	[7]
MAPbBr ₃	ZIF-8	degradation of organic pollutants	2019	[8]
MAPbBr ₃	MA-Mn(HCOO) ₃	Solar cell	2020	[9]
CsPbBr ₃ / MAPbBr ₃	MIL-101 (Cr)	Tunable emission	2021	[10]

Explanation 1

The reason for choosing CsPbCl₂Br is that in our initial experiment, we tried CsPbCl_{3-x}Br_x (x=0~3) and recorded the performance data when x was set to different values. We found that when x=0~1, the material was very unstable and easy to fluorescence quenching. But when X>1, with the increase of x, the spectrum will gradually red-shift and the lifetime will also gradually increase, which is contrary to the pursuit of ultra-fast scintillation. Therefore, we decided to choose CsPbCl₂Br in consideration of scintillation performance and material stability. Specific implementation methods and experimental data analysis are as follows.

CsPbCl₃@MOF(x=0):

Dissolve 2.8 mg PbCl₂ in 1mL DMF, stir at 100 degrees until completely dissolved, then disperse 15mg MOF powder in it, stir fully for 12 hours to ensure part of PbCl₂ into the MOF cages. The supernatant was removed and PbCl₂ that did not enter the cages were washed away. Finally, PbCl₂@MOF powder was obtained and dissolved in 1mL toluene solution for later use. 84 mg CsCl (0.5mmol) was dissolved in 1 mL methanol and stirred at 60°C until completely dissolved as the precursor solution. PbCl₂@MOF, previously dispersed with toluene, was transferred into a beaker and stirred vigorously. Then 30 μL CsCl precursor was quickly dropped into the beaker with a pipette gun. After intense stirring, washing and drying, CsPbCl₃@MOF powder was finally obtained.

CsPbCl₂Br@MOF(x=1):

Dissolve 2.8 mg PbCl₂ in 1mL DMF, stir at 100 degrees until completely dissolved, then disperse 15mg MOF powder in it, stir fully for 12 hours to ensure part of PbCl₂ into the MOF cages. The supernatant was removed and PbCl₂ that did not enter the cages were washed away. Finally, PbCl₂@MOF powder was obtained and dissolved in 1mL toluene solution for later use. 106 mg CsBr (0.5mmol) was dissolved in 1 mL methanol and stirred at 60°C until completely dissolved as the precursor solution. PbCl₂@MOF, previously dispersed with toluene, was transferred into a beaker and stirred vigorously. Then 30 μL CsBr precursor was quickly dropped into the beaker with a pipette gun. After intense stirring, washing and drying, CsPbCl₂Br@MOF powder was finally obtained.

CsPbClBr₂@MOF(x=2):

Dissolve 3.6 mg PbBr₂ in 1mL DMF, stir at 100 degrees until completely dissolved, then disperse 15mg MOF powder in it, stir fully for 12 hours to ensure part of PbBr₂ into the MOF cages. The supernatant was removed and PbBr₂ that did not enter the cages were washed away. Finally, PbBr₂@MOF powder was obtained and dissolved in 1mL toluene solution for later use. 84 mg CsCl (0.5mmol) was dissolved in 1 mL methanol and stirred at 60°C until completely dissolved as the precursor solution. PbBr₂@MOF, previously dispersed with toluene, was transferred into a beaker and stirred vigorously. Then 30 μL CsCl precursor was quickly dropped into the beaker with a pipette gun. After intense stirring, washing and drying, CsPbCl₂Br@MOF powder was finally obtained.

CsPbBr₃@MOF(x=3):

Dissolve 3.6 mg PbBr₂ in 1mL DMF, stir at 100 degrees until completely dissolved, then disperse 15mg MOF powder in it, stir fully for 12 hours to ensure part of PbBr₂ into the MOF cages. The supernatant was removed and PbBr₂ that did not enter the cages were washed away.

Finally, $\text{PbBr}_2@MOF$ powder was obtained and dissolved in 1mL toluene solution for later use. 106 mg CsBr (0.5mmol) was dissolved in 1 mL methanol and stirred at 60°C until completely dissolved as the precursor solution. $\text{PbBr}_2@MOF$, previously dispersed with toluene, was transferred into a beaker and stirred vigorously. Then $30\ \mu\text{L}$ CsBr precursor was quickly dropped into the beaker with a pipette gun. After intense stirring, washing and drying, $\text{CsPbBr}_3@MOF$ powder was finally obtained.

According to **Figure S4(a)(b)**, both spectrum and life are $\text{CsPbCl}_2\text{Br}@MIL-101(\text{Cr})$, which better meet the requirements of ultrafast scintillation. In addition, according to the TEM image of $\text{CsPbBr}_3@MIL-101(\text{Cr})$ in **Figure S4(c)**, it can be observed that CsPbBr_3 is difficult to disperse evenly in the MOF structure due to its large diameter (about 5nm), and the filling rate is not high. Therefore, considering the stability, luminescence characteristics and fast transient life of PeQDs, CsPbCl_2Br quantum dots were selected to be assembled in MOF.

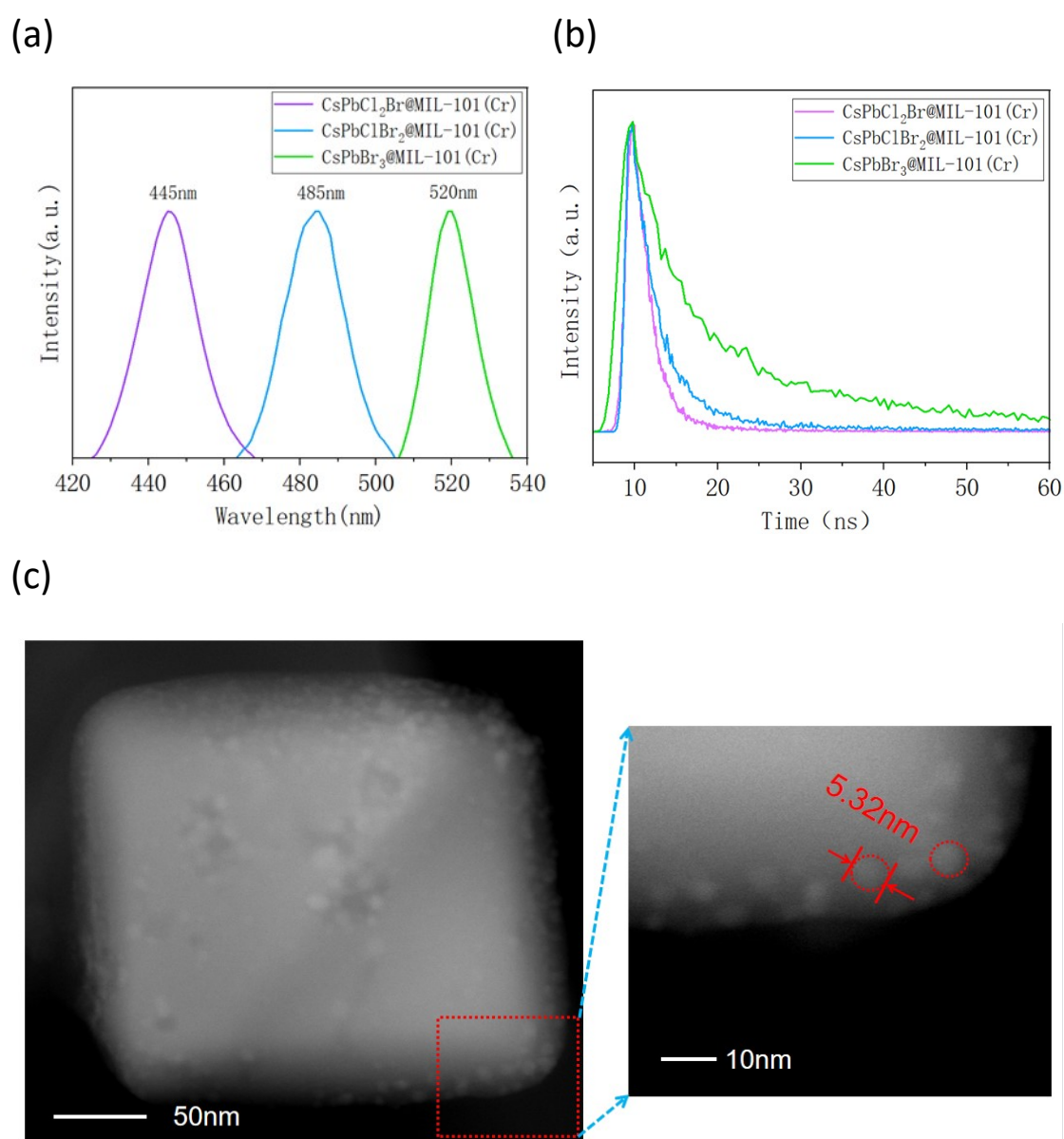


Figure S4 (a) The PL data of $\text{CsPbCl}_{3-x}\text{Br}_x @MIL-101(\text{Cr})$ at different values of x . (b) The Transient lifetime of $\text{CsPbCl}_3-x\text{Br}_x @MIL-101(\text{Cr})$ at different values of x . (c) TEM images of $\text{CsPbBr}_3 @MIL-101(\text{Cr})$

Explanation 2

The unit body free energy (ΔG_B) is proportional to the logarithm of the saturation ratio (S , defined as $S = C/C_s$), so ΔG_B increases as S increases. As formula $\Delta G = \Delta G_V + \Delta G_S = \frac{4}{3}\pi r^3 \Delta G_B + 4\pi r^2$, the increase of supersaturation ratio S leads to the increase of absolute value of ΔG_V , and ΔG_V is negative, so ΔG^*_{Hom} decreases, as shown in the **Figure S5**. The influence of supersaturation ratio S on ΔG^*_{Hom} is reflected in the change of luminescence intensity in the preparation of perovskite. When the precursor CsBr solution is further dropped, the luminescence intensity of the material is obviously stronger, indicating that more perovskite is generated.

The critical nucleus radius r_0 is defined as $d(\Delta G)/dr = 0$, and the nucleation energy barrier ΔG^*_{Hom} is the value of G when $r = r_0$ ($\Delta G^*_{Hom} = \frac{4}{3}\pi r_0^3 \Delta G_B + 4\pi r_0^2$). If the size of the nucleus is larger than r_0 , thermal fluctuations induced clusters will be thermodynamically stable and tend to grow further as nucleation centers. To reach the critical nucleation radius r_0 , an energy beyond the nucleation energy barrier ΔG^*_{Hom} is required to drive the thermodynamic process.

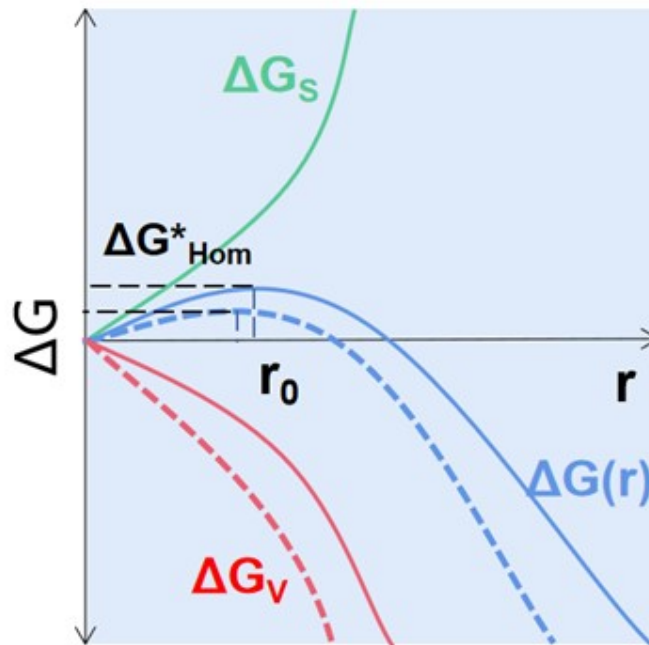


Figure S5 The influence of S on ΔG_V , ΔG and ΔG^*_{Hom}

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