Monodisperse Bismuth-Halide Double Perovskite Nanocrystals Confined in Mesoporous Silica Templates

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Synthesis of mesoporous silica templates

KIT-6 A mixture of 2 g P123 (Aldrich，$EO_{20}PO_{70}EO_{20}$，Ma=5800), 5 ml (12 M) HCl and 108.5 ml water was stirred well in a beaker at room temperature (35 ℃). Then, 3.75 ml *N*-butyl alcohol was added and continuous stirred for 1 h before adding 6.9 ml TEOS, and the second mixture was stirred for 24 h at 35 ℃before transferring into a Teflon bottle and heating at 100 ℃ for 24 h in the oven. The final product was got by filtering, washing with water, drying at room temperature and calcining in muffle furnace at 550℃for 6 h.

SBA-15 4.0 g P123 was dissolved by stirring vigorously in a solution of 126 mL deionized water and 24 ml (2 M) HCl, then 9.2 ml TEOS wad added into the solution. After stirring for 24 h at 40 ℃, the mixture was transferred into a Teflon bottle and heated at 100 ℃ for 24 h. After the reaction, the product was filtered, washed with water and dried at 60 ℃, and then calcined in muffle furnace at 550 ℃.

MCM-41 2 g CTAB was dissolved in a solution of 100 ml water and 8.8 ml 45% $NH_3 \cdot H_2O$, then 8.3 ml TEOS was injected into the mixture with an injection pump for 1 h. The solution was stirred for 24 h at room temperature, the gel solution was transferred into a Teflon bottle and crystallized at 100 ℃ for 24 h. Finally, the product was obtained through filtering, washing with water, drying at 60 ℃ and calcining in muffle furnace at 550 ℃for 6 h.

The phase and purity of above three templets were proved by SAXS data in Figure S4-6, their BET surface and pore size were carried out by physical adsorption/desorption experiments in Figure S7-12.

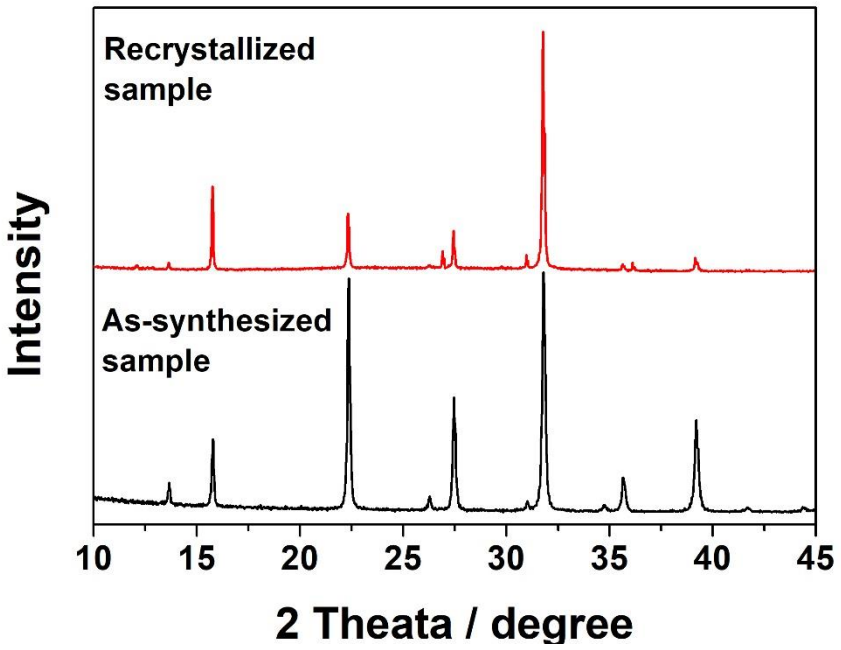

Figure S1. PXRD of the as-synthesized and recrystallized samples of **1**.

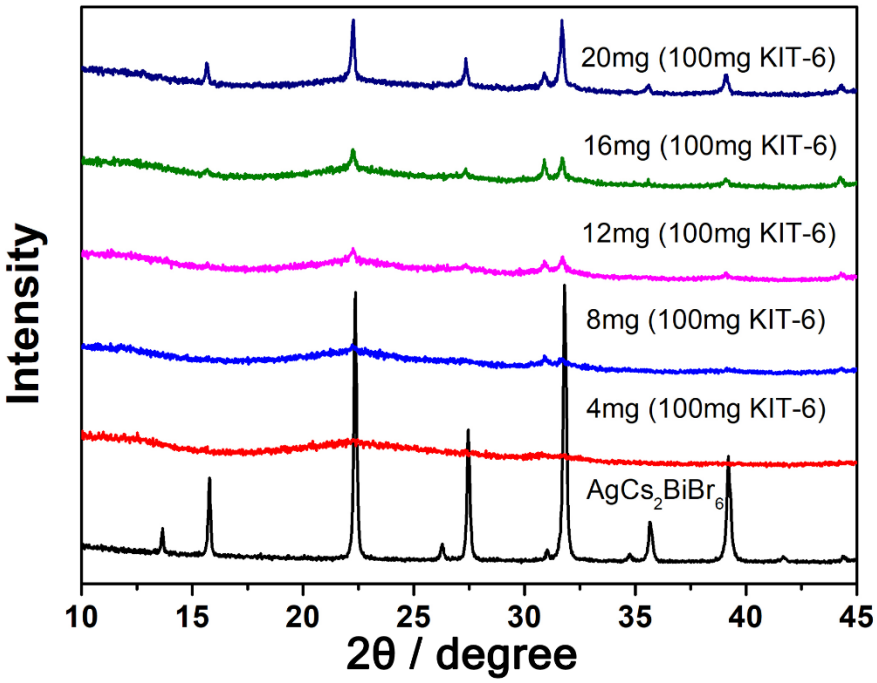

Figure S2. PXRD of **1**@KIT-6 with different loading amount.

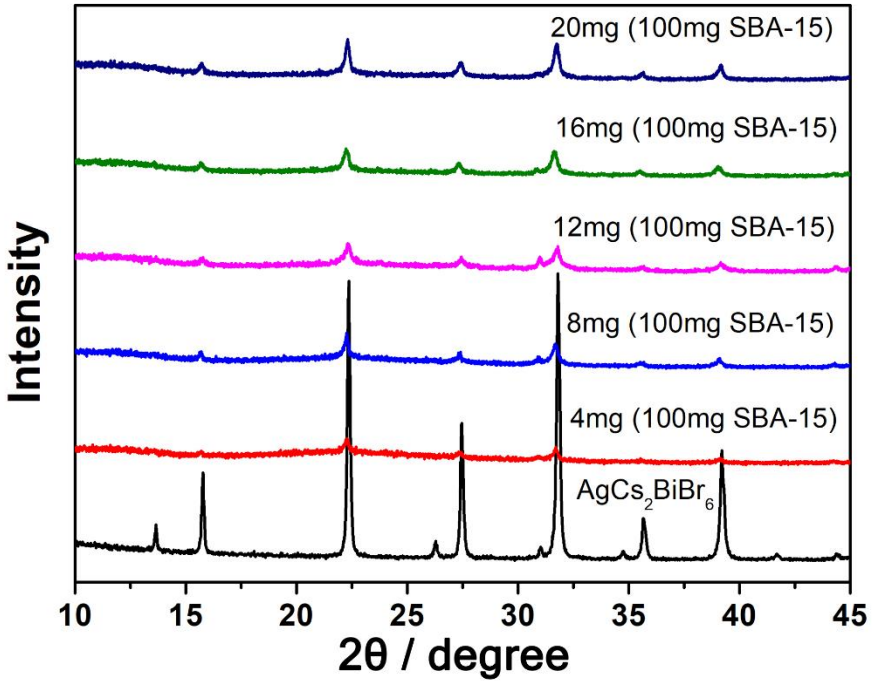

Figure S3. PXRD of **1**@SBA-15 with different loading amount.

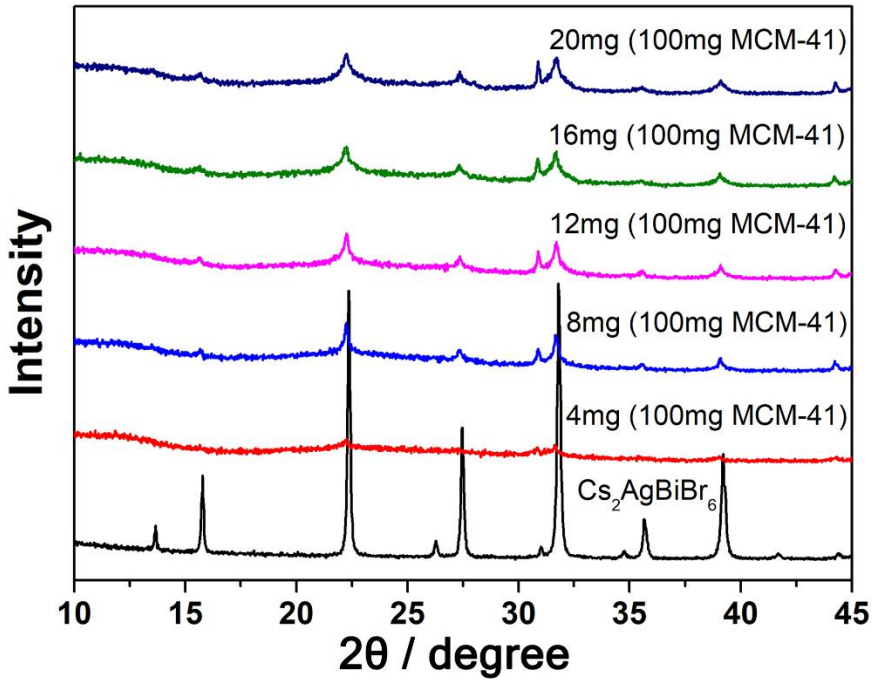

Figure S4. PXRD of **1**@MCM-41 with different loading amount.

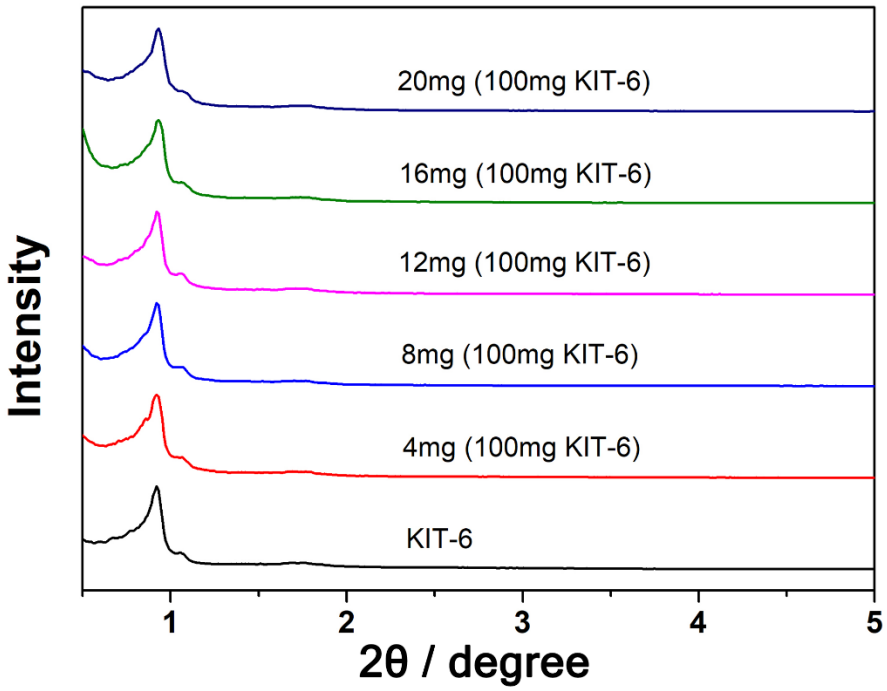

Figure S5. SAXS of **1**@KIT-6 with different loading amount.

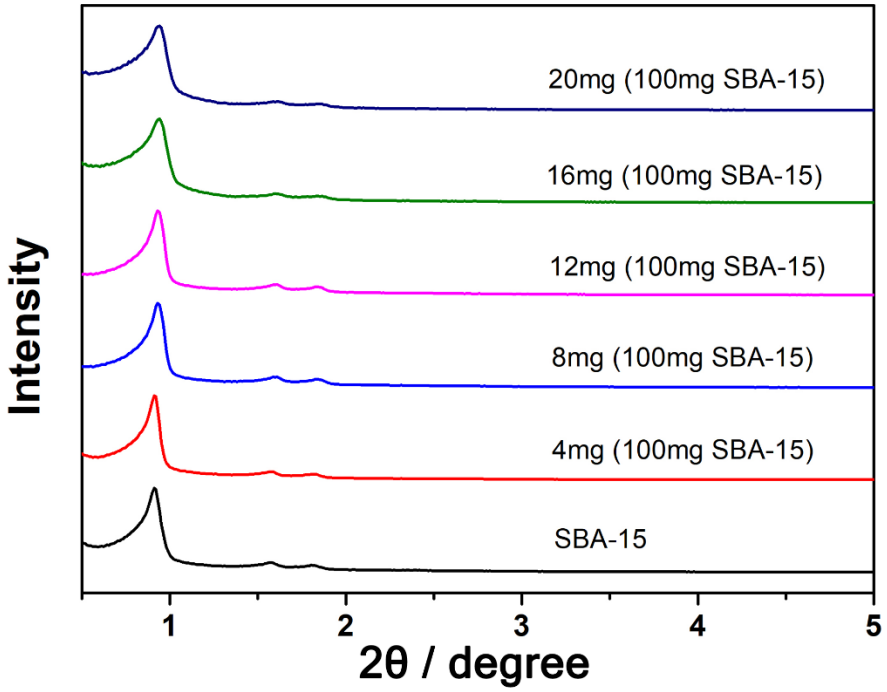

Figure S6. SAXS of **1**@SBA-15 with different loading amount.

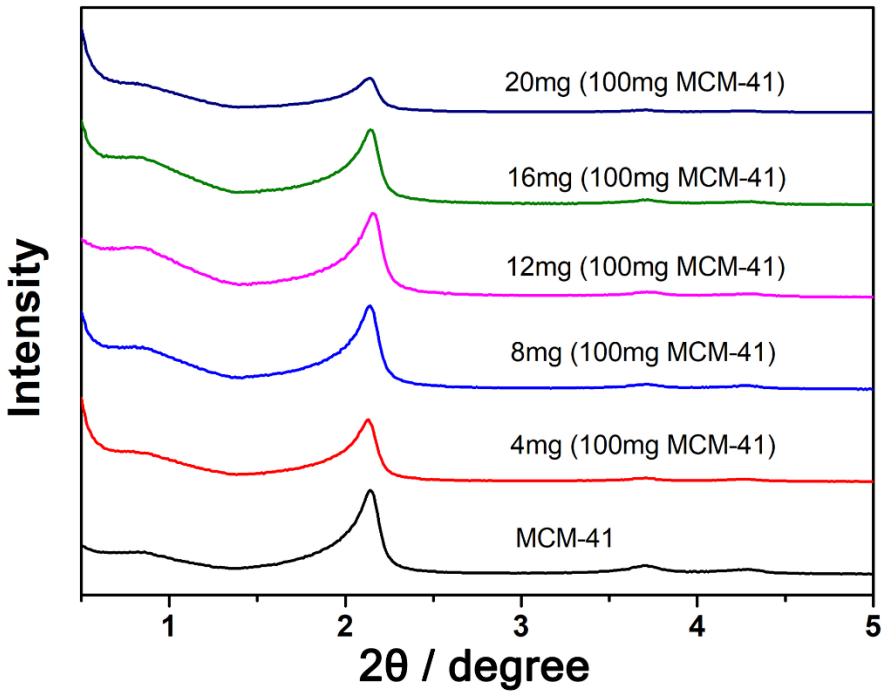

Figure S7. SAXS of **1**@MCM-41 with different loading amount.

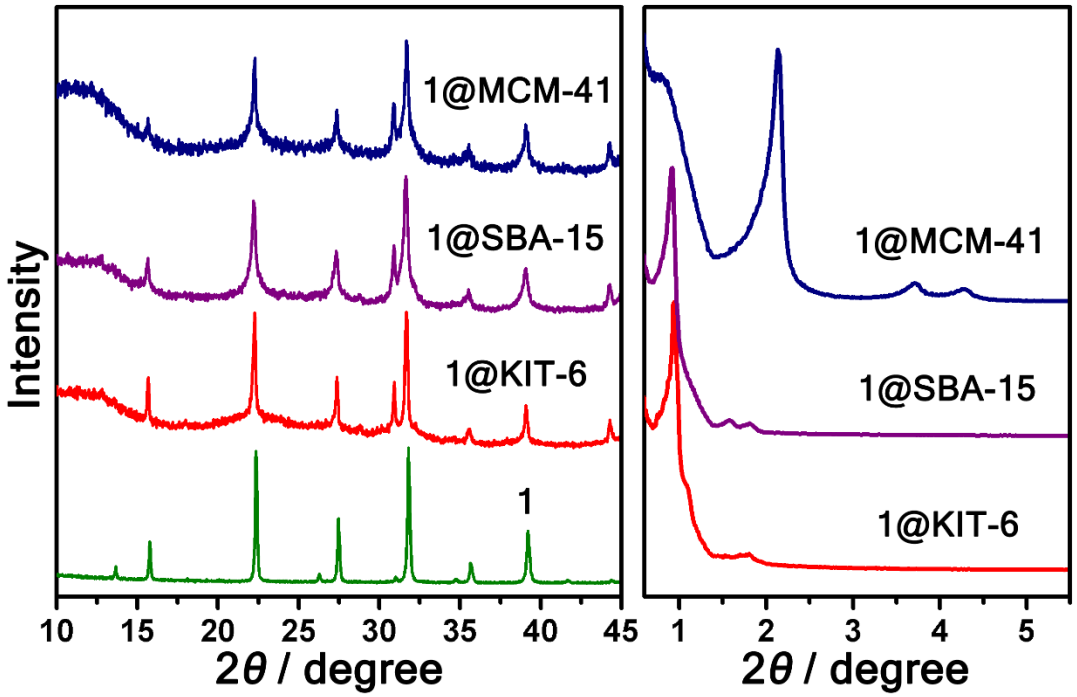

Figure S8. Stability of **1**@KIT-6, **1**@SBA-15, **1**@MCM-41. The newly prepared samples were kept in air with relative humidity of 55 % for 180 days, and the PXRD patterns of 1@KIT-6, 1@SBA-15, 1@MCM-41 after moisture showed no evidence of material decomposition, which proves the high stability of the samples.

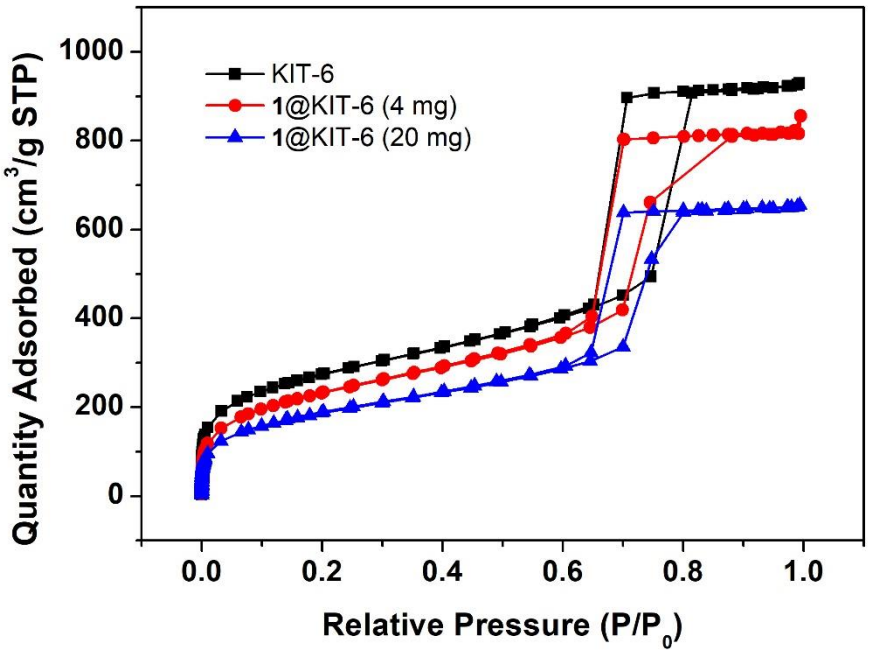

Figure S9. N_2 adsorption/desorption data of KIT-6 and **1**@KIT-6 with different loading amount.

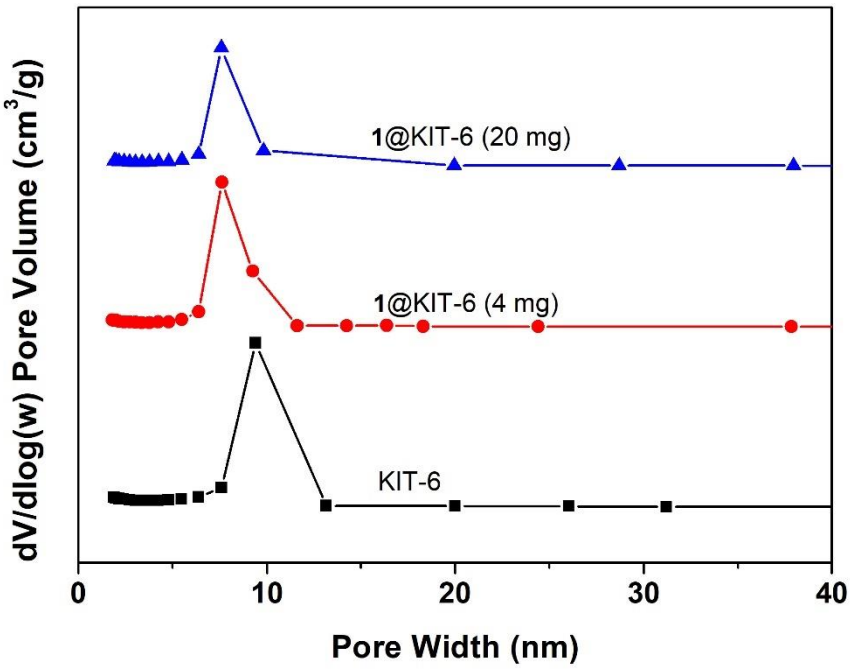

Figure S10. Pore size distribution of KIT-6 and **1**@KIT-6 with different loading amount.

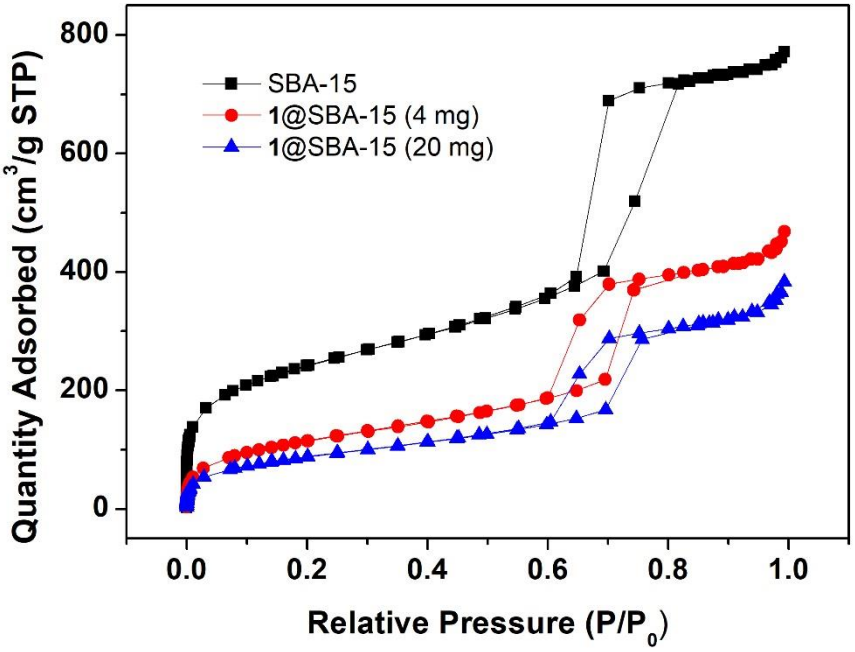

Figure S11. N_2 adsorption/desorption data of SBA-15 and **1**@SBA-15 with different loading amount.

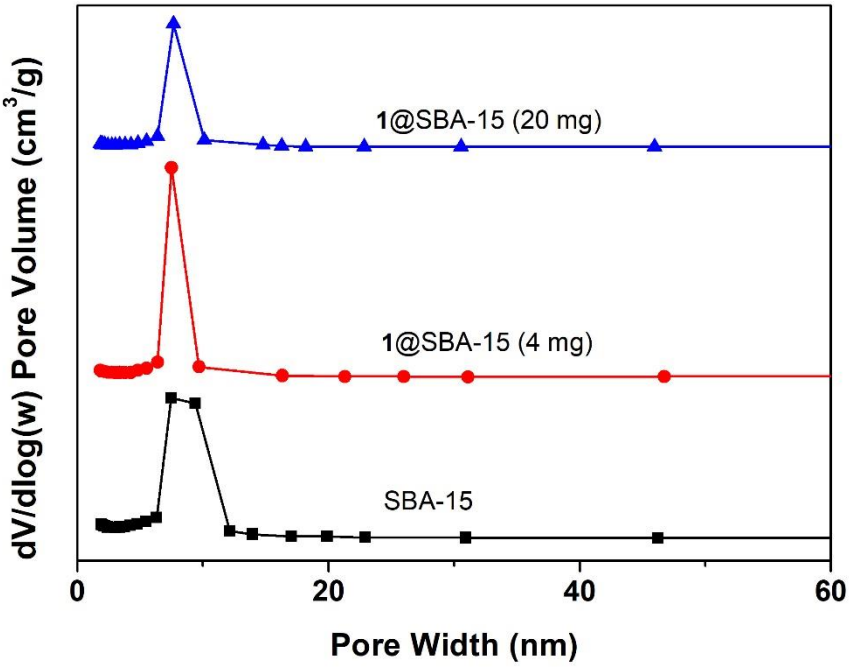

Figure S12. Pore size distribution of SBA-15 and **1**@SBA-15 with different loading amount.

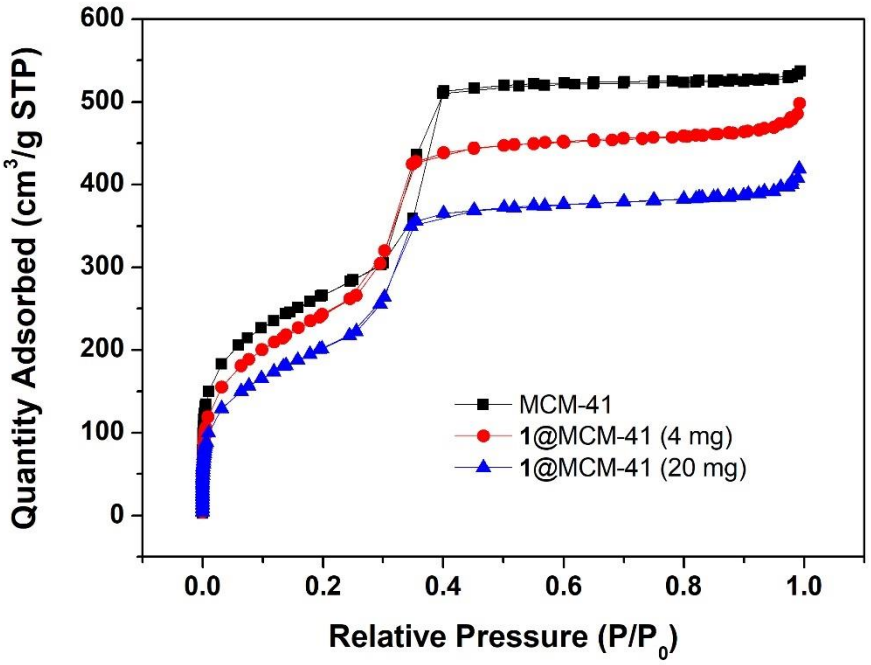

Figure S13. N_2 adsorption/desorption data of MCM-41 and **1**@MCM-41 with different loading amount.

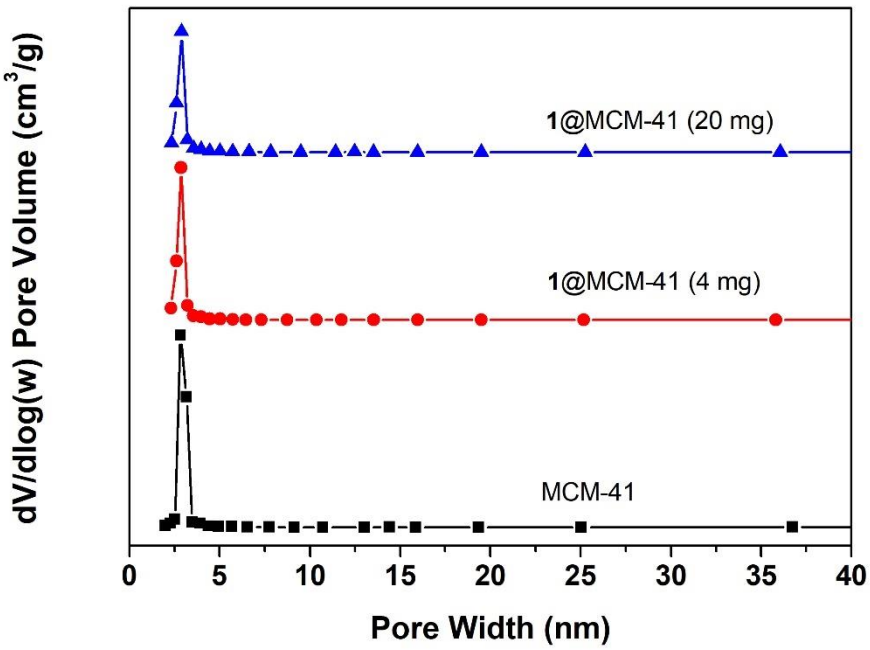

Figure S14. Pore size distribution of MCM-41 and **1**@MCM-41 with different loading amount.

Table S1. Comparison of specific surface area and pore size of mesoporous silicon before and after loading samples.

Sample	BET surface (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
KIT-6	971	1.44	5.92
1@KIT-6 (4 mg)	853	1.33	6.02
1@KIT-6 (20 mg)	675	1.01	6.12
SBA-15	857	1.19	5.66
1@SBA-15 (4 mg)	530	1.02	5.72
1@SBA-15 (20 mg)	425	0.81	5.81
MCM-41	954	0.83	2.99
1@MCM-41 (4 mg)	852	0.76	3.02
1@MCM-41 (20 mg)	753	0.72	3.07

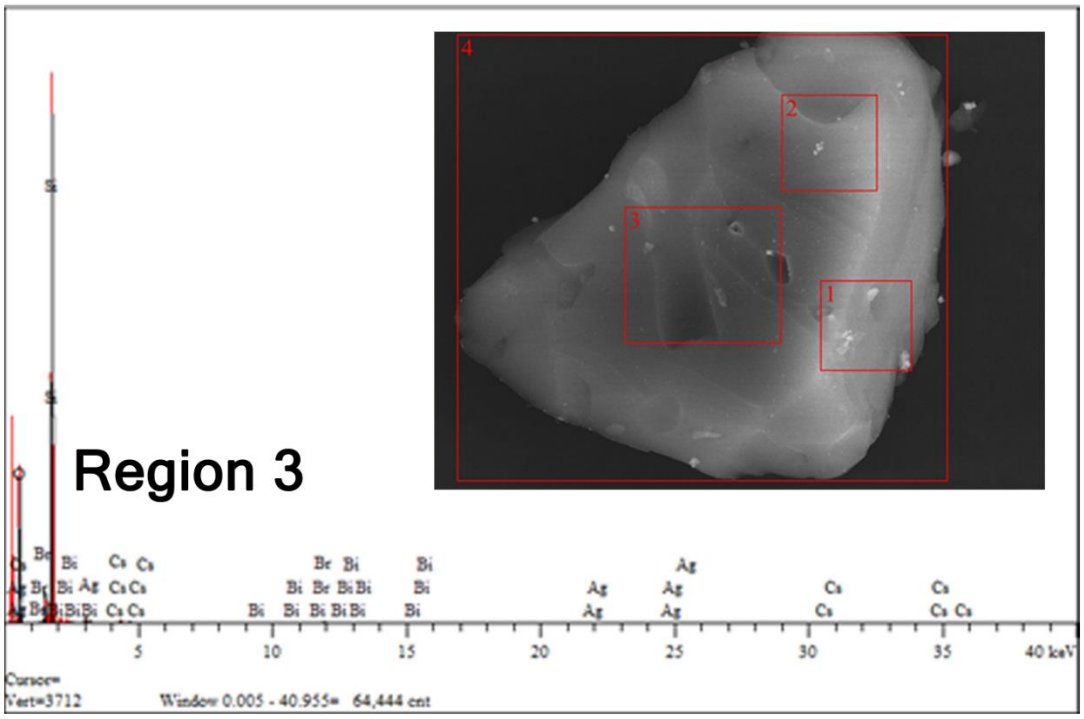

Figure S15. EDX image of **1**@KIT-6 (20 mg **1** in 100 mg KIT-6).

Table S2. EDX data of **1**@KIT-6 (20 mg **1** in 100 mg KIT-6).

Element	Region 1 Atomic %	Region 2 Atomic %	Region 3 Atomic %	Region 4 Atomic %
Cs	0.592	0.536	0.596	0.494
Ag	0.255	0.252	0.304	0.249
Bi	0.269	0.265	0.315	0.238

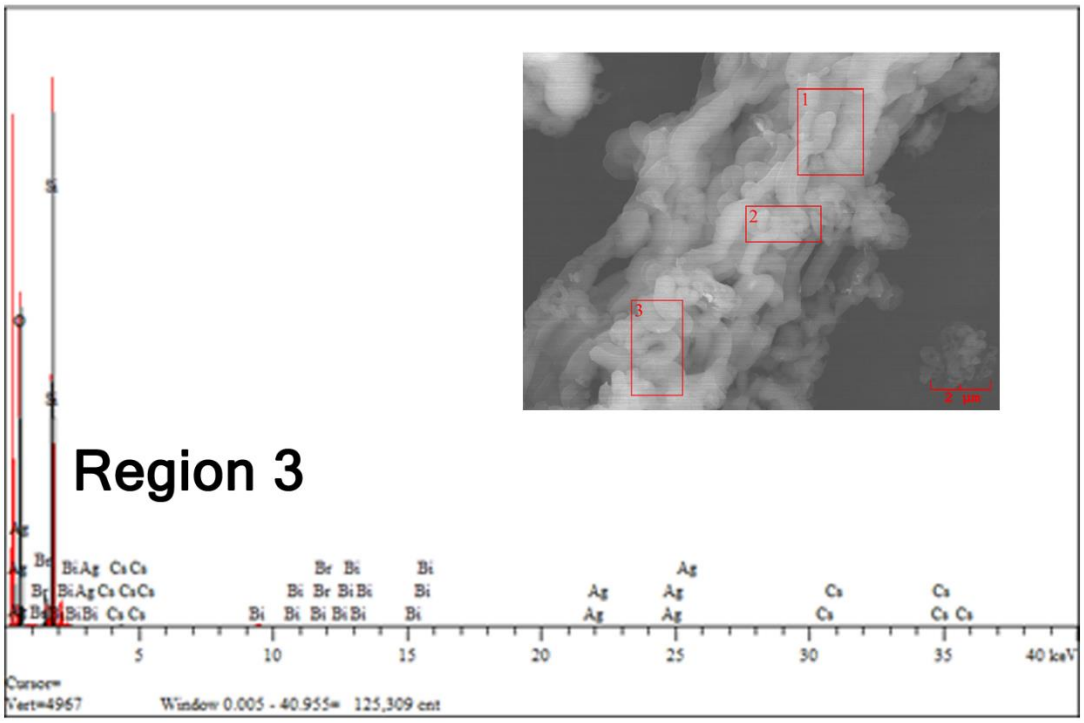

Figure S16. EDX image of **1**@SBA-15 (20 mg **1** in 100 mg SBA-15).

Table S3. EDX data of **1**@SBA-15 (20 mg **1** in 100 mg SBA-15).

Element	Region 1 Atomic %	Region 2 Atomic %	Region 3 Atomic %
Cs	0.437	0.473	0.573
Ag	0.211	0.244	0.273
Bi	0.224	0.273	0.296

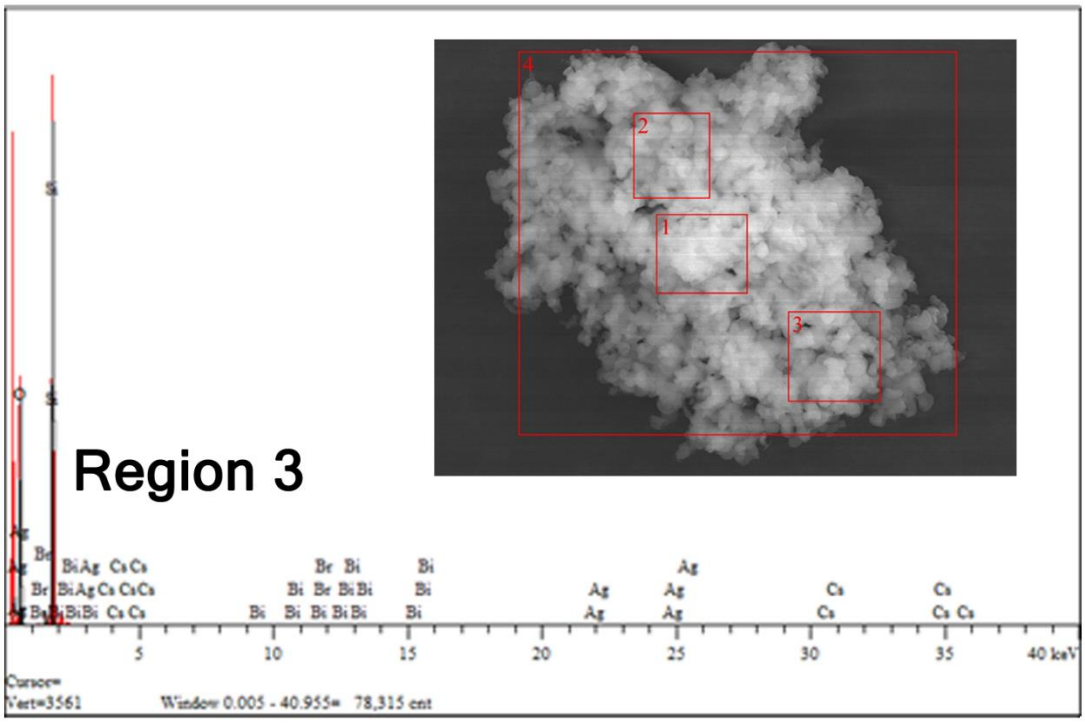

Figure S17. EDX image of **1**@MCM-41 (20 mg **1** in 100 mg MCM-41).

Table S4. EDX data of **1**@MCM-41 (20 mg **1** in 100 mg MCM-41).

Element	Region 1 Atomic %	Region 2 Atomic %	Region 3 Atomic %	Region 4 Atomic %
Cs	0.195	0.174	0.213	0.184
Ag	0.111	0.089	0.104	0.106
Bi	0.098	0.096	0.105	0.090

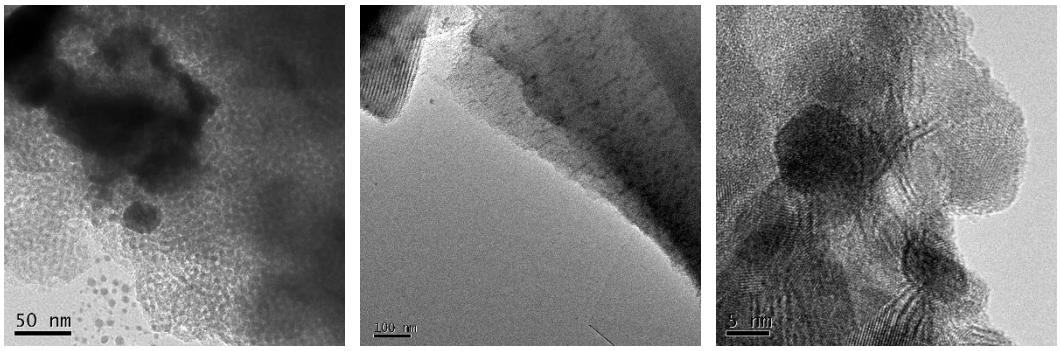

Figure S18. TEM images of **1**@KIT-6 (left), **1**@SBA-15 (middle) and **1**@MCM-41 (right). In order to prove the morphology of our samples, we extend the time when the electron beam hit the samples. As shown in Figure S18 left, SiO_2 on KIT-6 will be destroyed or even "dissolved" by long-term electron beam bombardment. However, complex **1**, which is composed of heavy metal ions and halogens, can remain crystalline even after being bombarded by electron beams for a long time. We can see from the figure that there is a clear gap between the nanocrystals of **1**, that is, the destroyed SiO_2. It can be inferred that the nanocrystals of **1** are monodisperse nanocrystals separated by SiO_2. At the same time, because SiO_2 is dissolved at the edge of the material, the nanocrystals will detach from the channel, which is just proof of that. For **1**@SBA-15 (Figure S18 middle), we can see in the picture that there are indeed two kinds of nanocrystals: 0D (shorter) and 1D (longer) in the channel of SBA-15. These nanocrystals are separated by SiO_2 and are also monodisperse nanocrystals. For **1**@MCM-41 (Figure S18 right), we can also see that one-dimensional nanocrystals are separated by SiO_2 to form monodisperse 1D nanowires.

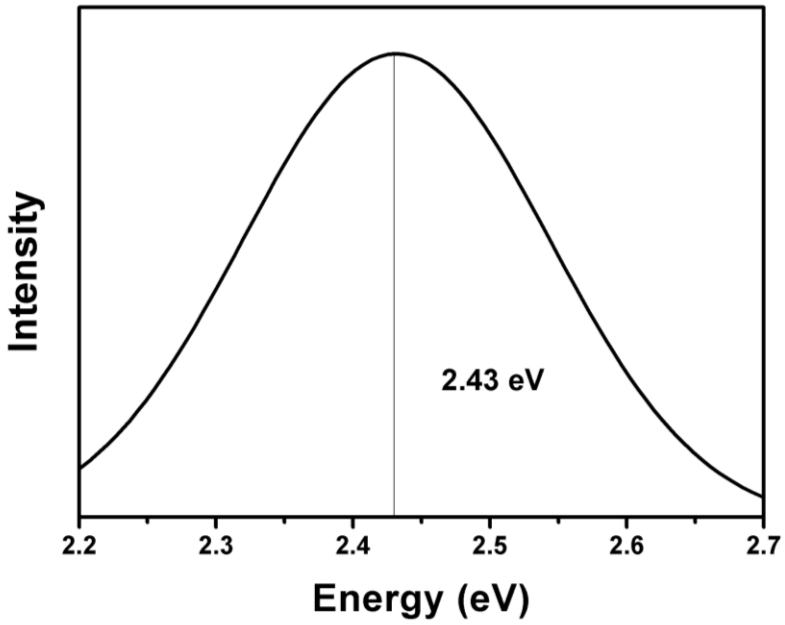

Figure S19. PL data of **1**@SBA-15 at 77 K.

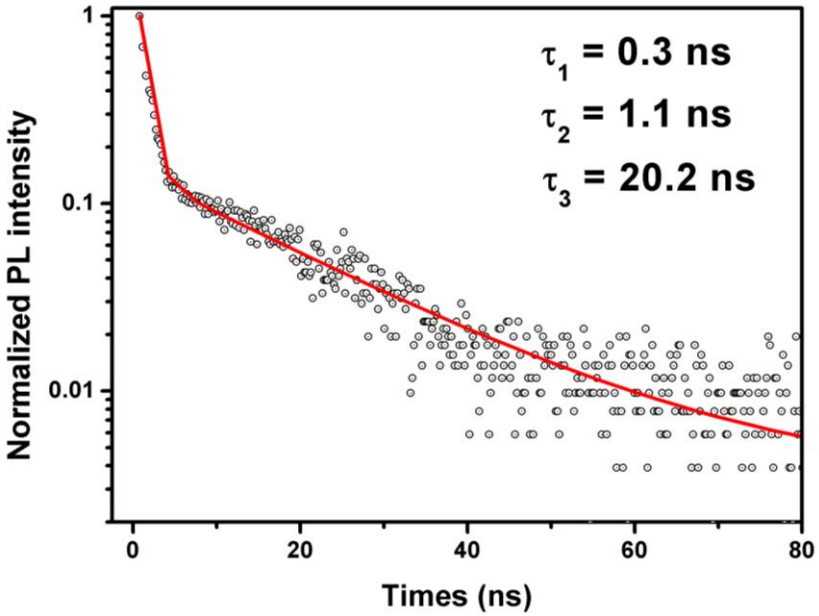

Figure S20. Fluorescence lifetime of **1**@SBA-15. This sample have three processes: a short-lifetime process (τ_1 = 0.3 ns), an intermediate-lifetime process (τ_2 = 1.1 ns) and a long-lived component (τ_3 = 20.2 ns).

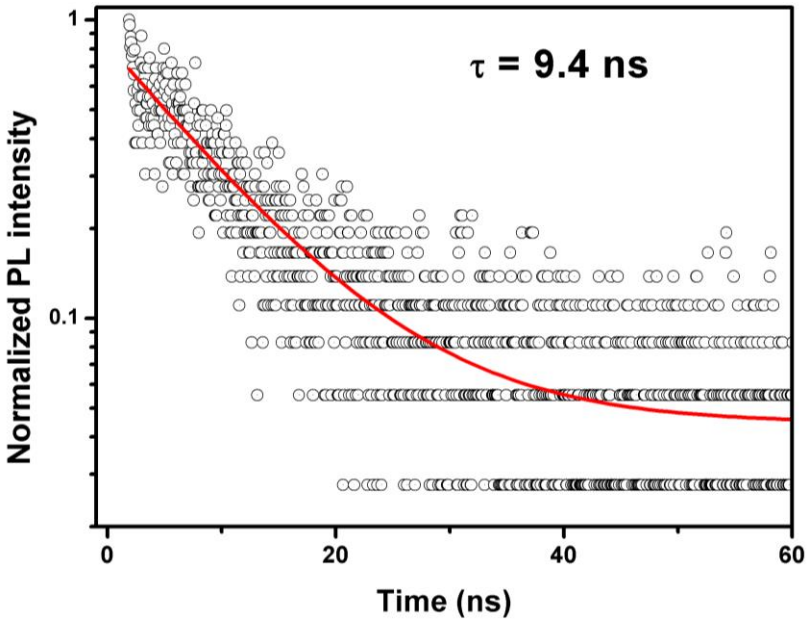

Figure S21. Fluorescence lifetime of **1**@MCM-41. This sample only have one processes: a long-lived component (τ = 9.4 ns). Compared with **1**@KIT-6 and **1**@SBA-15, the short-life and intermediate-life processes of nanocrystals in **1**@MCM-41 have not been observed, which may be due to the size of nanocrystals in **1**@MCM-41 is smaller than that of **1**@KIT-6 and **1**@SBA-15 samples.