ELECTRONIC SUPPORTING INFORMATION

New Journal of Chemistry

Incorporation of methylene blue into mesoporous silica nanoparticles for singlet oxygen generation

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Syntheses of LUS materials (type MCM-41)

Synthesis of p_{wa}-MB@LUS. First, LUS-TMA (MCM-41 type of silica with tetramethylammonium ions) was prepared according to previous works from our group.[1,2] Then 1g LUS-TMA and 4mg methylene blue trihydrate were dissolved in 50 mL water and stirred at 80 °C for 1h. The solution was filtered and washed twice with 50ml water for 3 times. The solid was dried at 80°C overnight.

Synthesis of p_{cy}-Ph@LUS. 1g LUS-TMA was heated to 130 °C under Ar. When the temperature reached 130 °C, the solid was kept under vacuum for 1h and then cooled to RT under Ar, yielding activated LUS-TMA. Then cyclohexane (15 mL) was added to the solid, followed by 0.026 mL of phenethyltrimethoxysilane. Afterwards more cyclohexane (45 mL) was added and the solution was stirred at 80 °C for 18h. Upon cooling, the mixture was filtered and the obtained solid was washed twice with 20 mL of cyclohexane, 20 mL of technical ethanol and 20 mL of acetone. The solid was dried at 80°C overnight.

Synthesis of p_{Wa},p_{Cy}-[0.1MB/Ph]@LUS. 0.5g p-Ph_{cy}@LUS and 2mg methylene blue trihydrate were dissolved in water (25 mL). The solution was stirred at 80 °C for 1h and then filtered and washed twice with 25mL water for 3 times. The solid was dried at 80°C overnight.

Synthesis of p_{Wa},p_{Cy}-[0.01MB/Ph]@LUS. The synthesis was similar to that of **p_{Wa},p_{Cy}-[0.1MB/Ph]@LUS** but using **p_{Cy}-Ph@LUS** prepared with a ten-fold amount (0.26 mL) of phenethyltrimethoxysilane.

Synthesis of p_{Cy},p_{Cy}-[0.1MB/Ph]@LUS. The same procedure as for the synthesis of p-Ph@LUS was first followed. Then 4 mg methylene blue trihydrate were added into the mixture and stirred at 80 °C for another 5h. Then the sample was filtered and washed twice with 20 mL of cyclohexane, 20 mL of technical ethanol and 20 mL of acetone. The solid was dried at 80°C overnight.

[1] B. Garcia-Cirera, M. Corbella, L. Bonneviot and B. Albela, *Microporous Mesoporous Mater.*, 2018, **261**, 150-157
[2] K. Zhang, B. Albela, M. Y. He, Y. M. Wang and L. Bonneviot, *Physical Chemistry Chemical Physics*, 2009, **11**, 2912-2921.

Figures

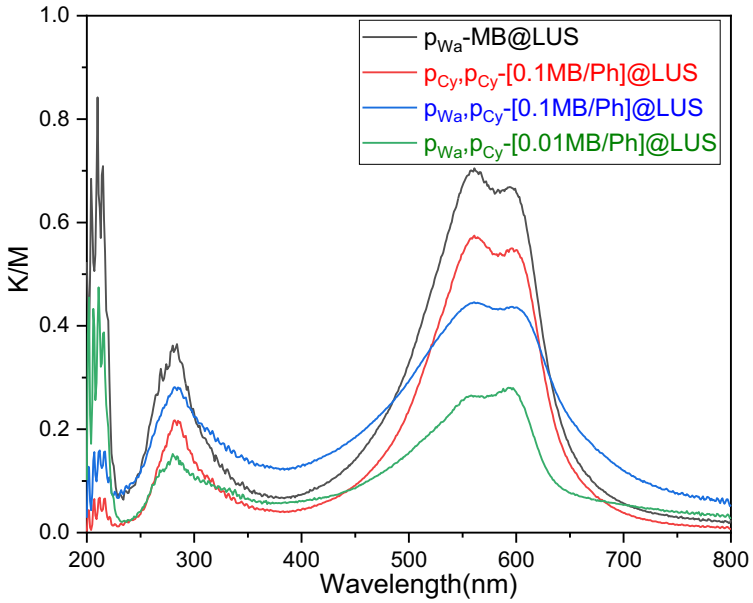


Fig. S1 Solid UV-Vis spectra of p_{Wa}-MB@LUS, p_{Cy}, p_{Cy}-[0.1MB/Ph]@LUS, p_{Wa}, p_{Cy}-[0.1MB/Ph]@LUS and p_{Wa}, p_{Cy}-[0.01MB/Ph]@LUS.

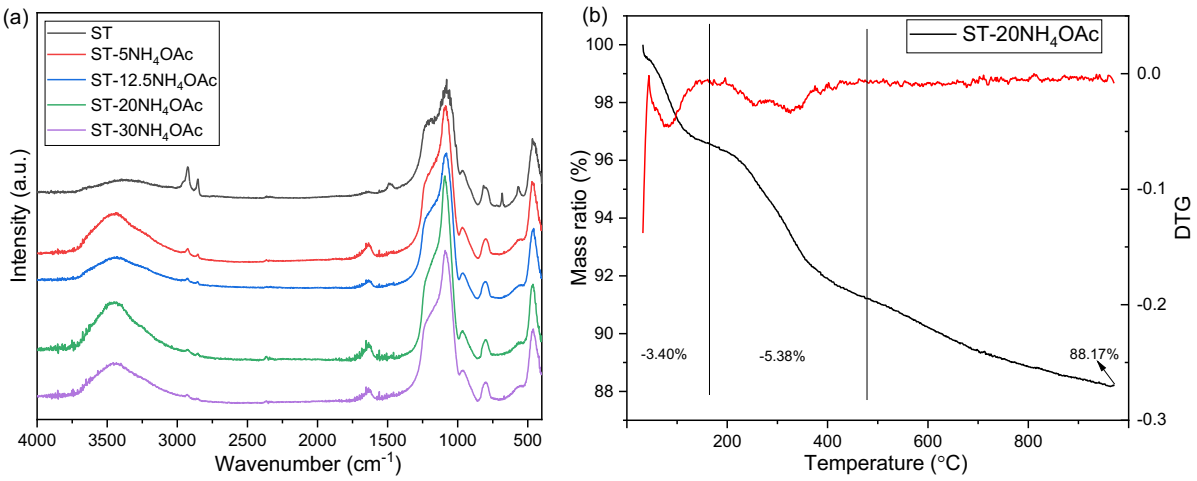


Fig. S2 (a) IR spectra of ST, ST-5NH_4OAc, ST-12.5NH_4OAc, ST-20NH_4OAc and ST-30NH_4OAc; (b) TGA analysis of ST-20NH_4OAc.

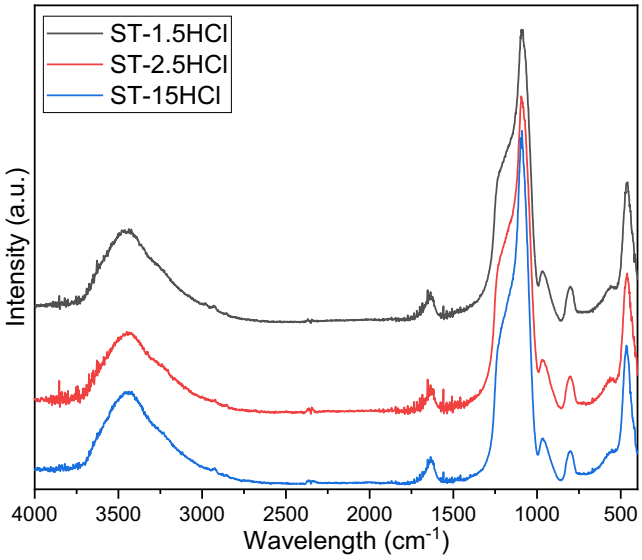


Fig. S3 IR spectra of extracted samples using HCl in EtOH/H_2O: ST-1.5HCl, ST-2.5HCl and ST-15HCl.

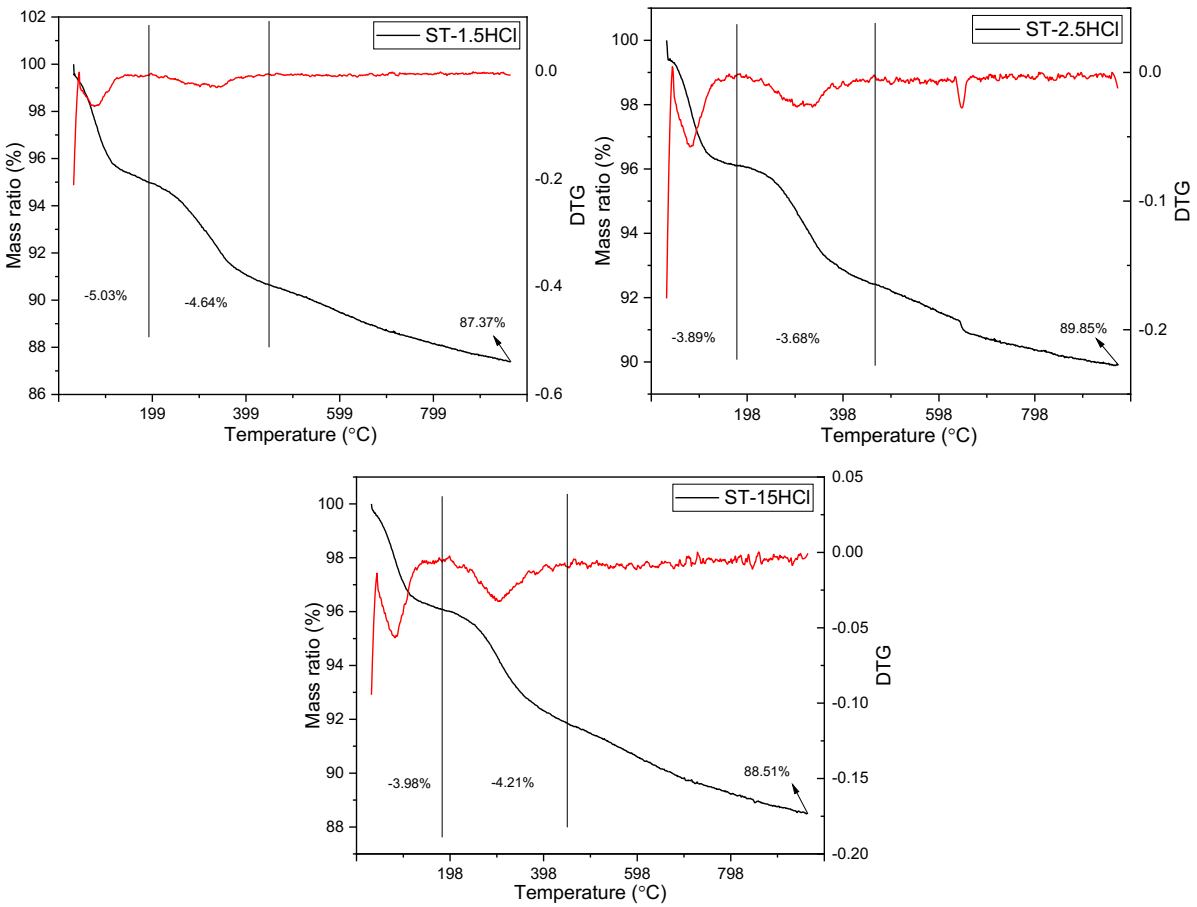


Fig. S4 TGA profiles of extracted samples using HCl in EtOH/H_2O: ST-1.5HCl, ST-2.5HCl and ST-15HCl.

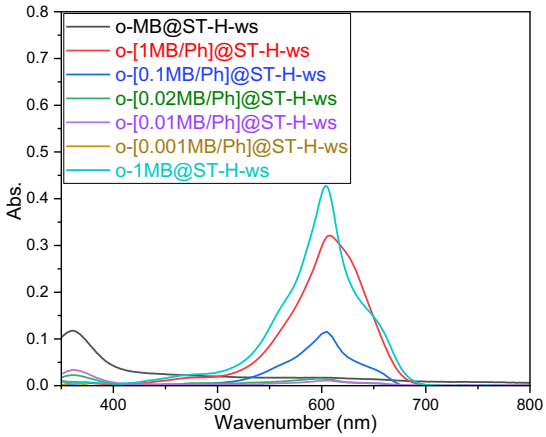


Fig. S5 UV-visible spectra of the solutions after extraction of the surfactant (HCl in a mixture of EtOH and H_2O) on "one-pot" samples.

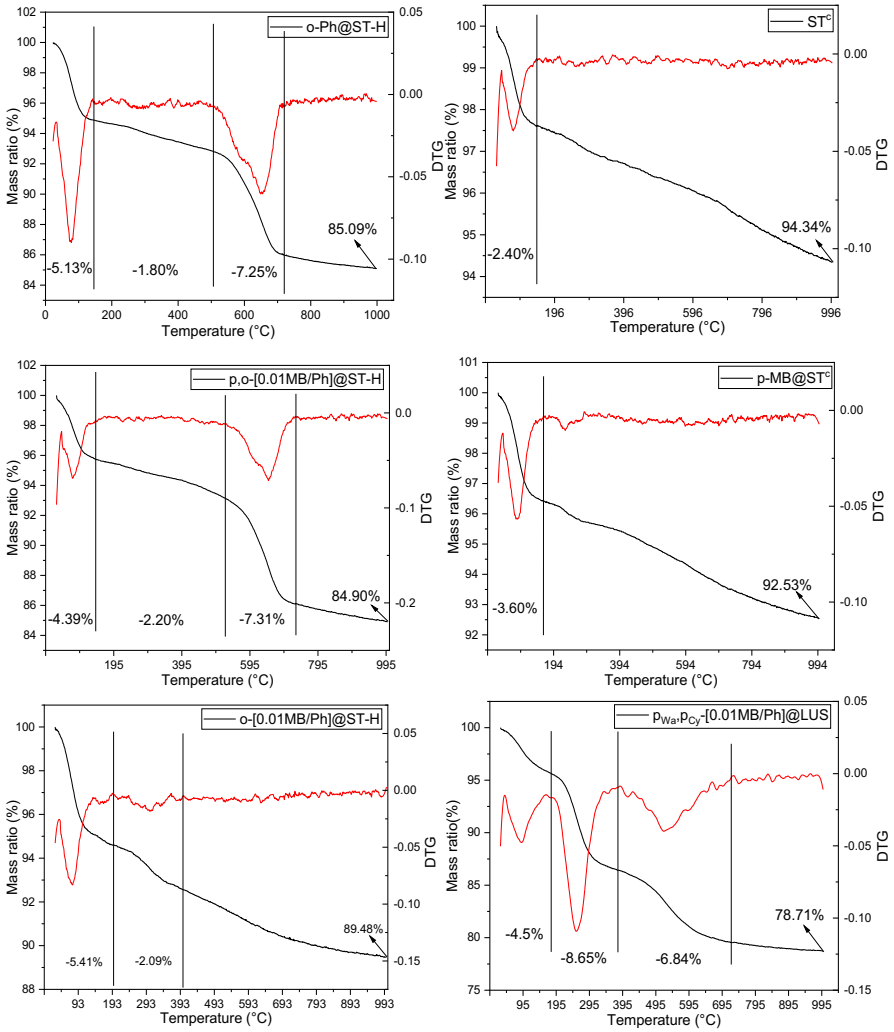


Fig. S6 TGA of o-Ph@ST-H, ST^c, p,o-[0.01MB/Ph]ST-H, p-MB@ST^c, o-[0.01MB/Ph]@ST-H and p_{Wa},p_{Cy}-[0.01MB/Ph]@LUS

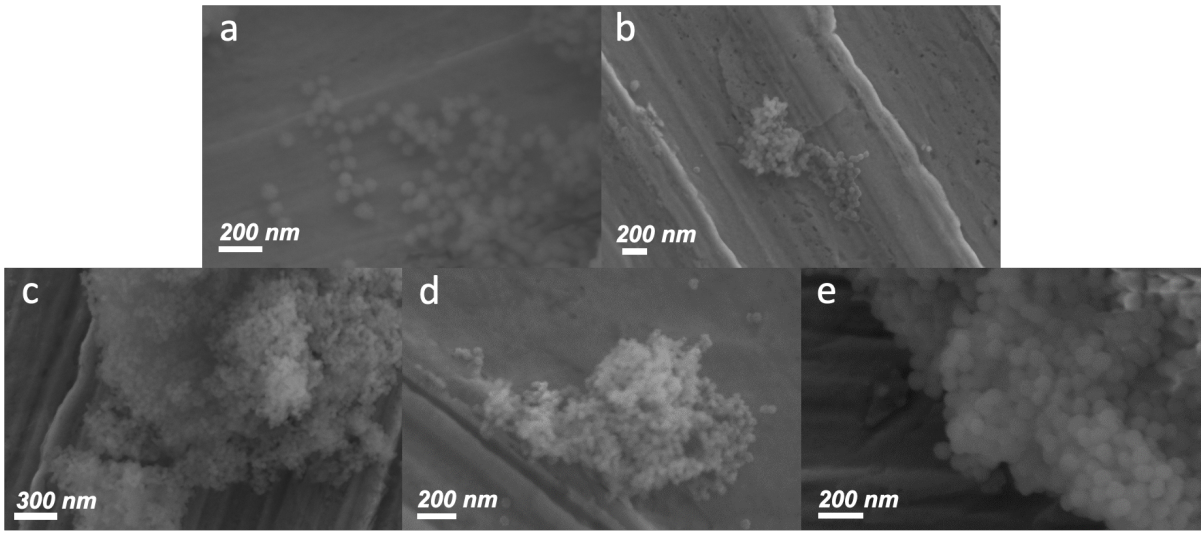


Fig. S7 SEM images of (a) o-Ph@ST-H, (b) o-[1MB/Ph]@ST-H, (c) o-[0.1MB/Ph]@ST-H, (d) o-[0.02MB/Ph]@ST-H and (e) o-[0.01MB/Ph]@ST-H.

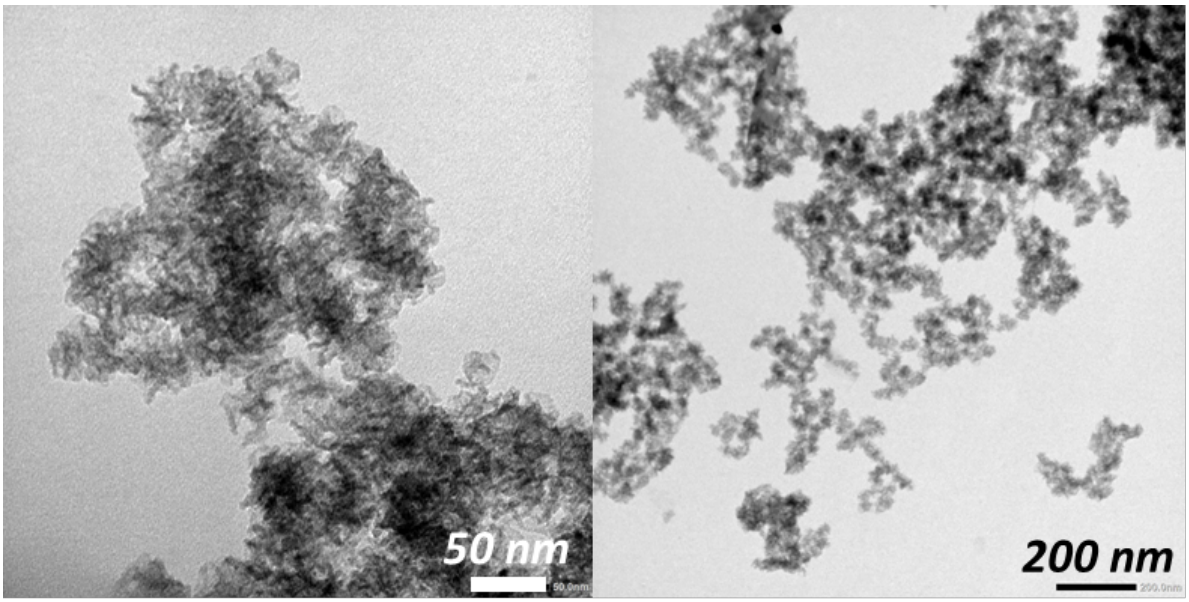


Fig. S8 TEM images of o-Ph@ST-H.

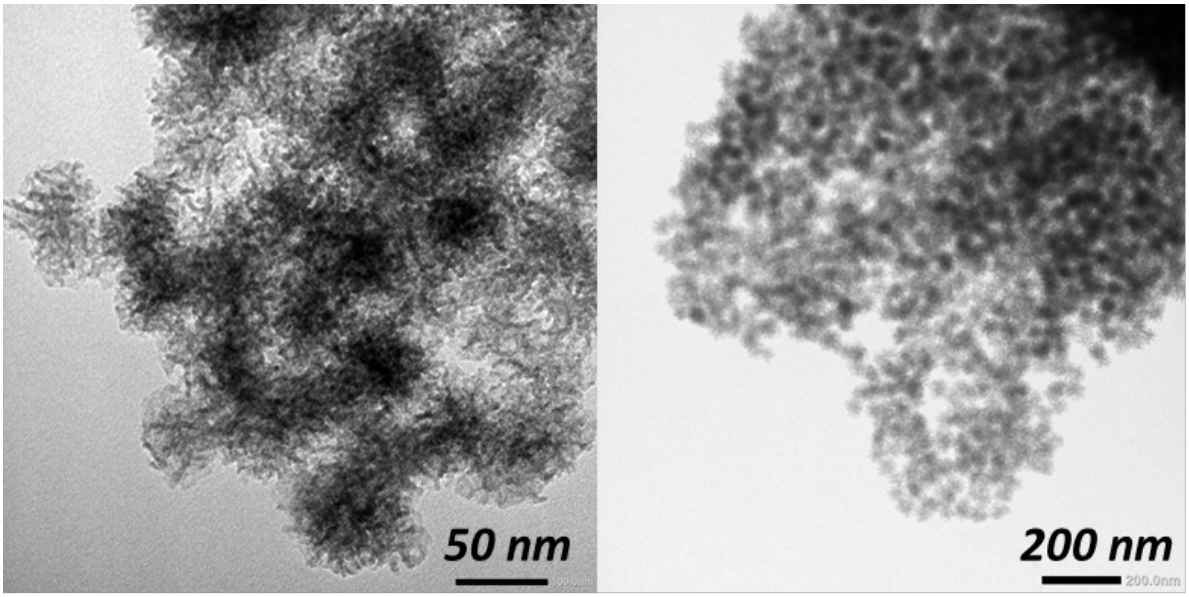


Fig. S9 TEM images of o-[0.01MB/Ph]@ST-H.

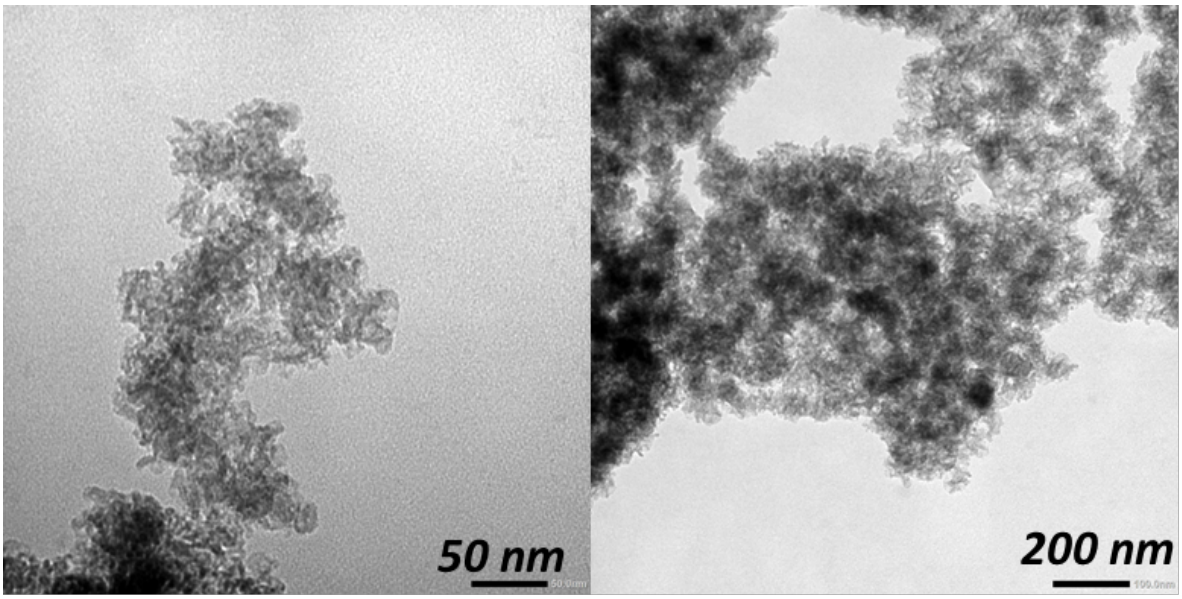


Fig. S10 TEM images of p,o-[0.01MB/Ph]@ST-H.

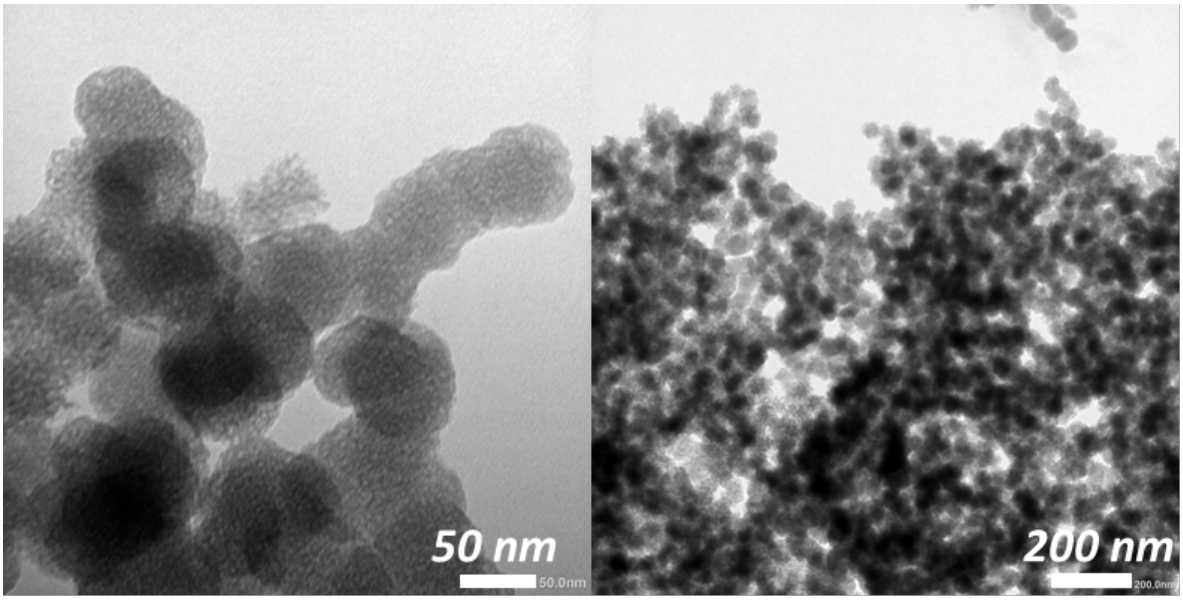


Fig. S11 TEM images of p-MB@ST^{c}.

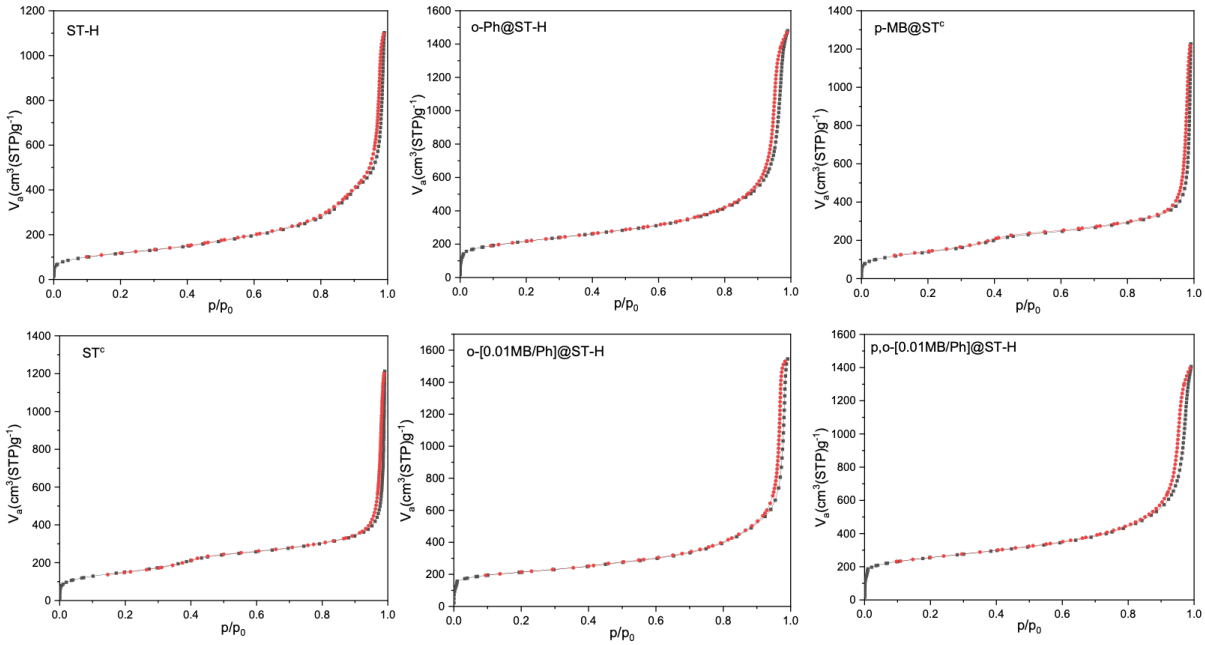
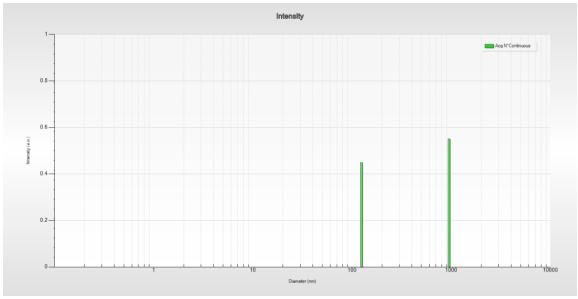


Fig. S12 Nitrogen sorption isotherms at 77 K of ST-H, ST^{c}, o-Ph@ST-H, o-[0.01MB/Ph]@ST-H, p-MB@ST^{c} and p,o-[0.01MB/Ph]@ST-H (See Table S2).

Pade Laplace *Acquisition: Continuous (Intensity) 00:02:15 24.99 °C*



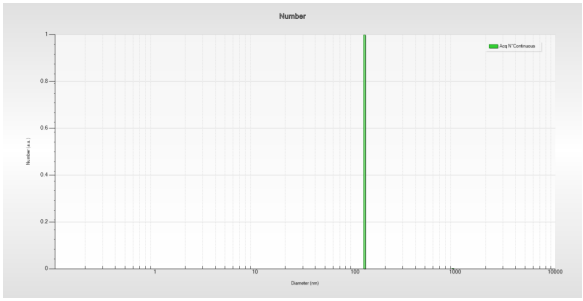
Dispersion statistics

Di 10%: *123.7 nm* ***Di 50%:*** *946.03 nm* ***Di 90%:*** *946.03 nm*
Mean Size(Intensity): *576.47 nm* ***Average count rate:*** *1656 kcps*

Detected size(s)

Size (nm)	Intensity	Decay Rate.	Diffusion Coeff. (m^2/s)
122.83	0.43	3378.08	64.78055E-013
956.47	0.53	433.82	83.19204E-014

Pade Laplace *Acquisition: Continuous (Number) 00:02:15 24.99 °C*



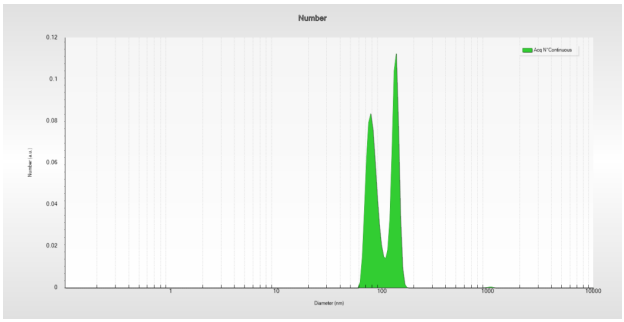
Dispersion statistics

Dn 10%: *123.7 nm* ***Dn 50%:*** *123.7 nm* ***Dn 90%:*** *123.7 nm*
Mean Size(Number): *124.66 nm*

Detected size(s)

Size (nm)	Number	Decay Rate.	Diffusion Coeff. (m^2/s)
122.83	1	3378.08	64.78055E-013

SBL *Acquisition: Continuous (Number) 00:02:15 24.99 °C*



Distribution statistics

Dn 10%: *71.02 nm* ***Dn 50%:*** *98.17 nm* ***Dn 90%:*** *142.11 nm*
Mean Size(Number): *106.05 nm*
Solution index: *8*

Peak : *1* ***Mode:*** *77.91 nm* ***Mean:*** *80.99 nm* ***Std Dev:*** *12.91 %* ***Intensity:*** *53.6 %*

Peak : *2* ***Mode:*** *135.68 nm* ***Mean:*** *132.33 nm* ***Std Dev:*** *8.82 %* ***Intensity:*** *46.4 %*

Fig. S13 DLS analysis of o-[0.01MB/Ph]@ST-H in methanol.

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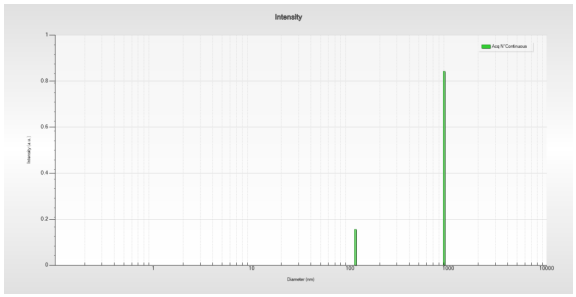


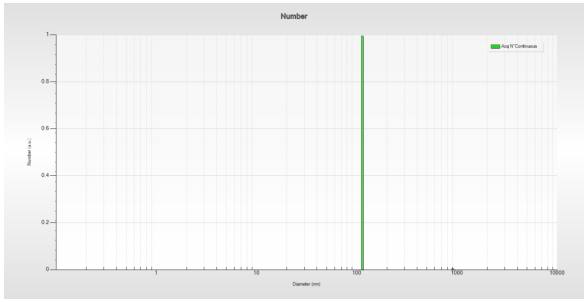
Dispersion statistics

Di 10%: *112.77 nm* ***Di 50%:*** *903.28 nm* ***Di 90%:*** *903.28 nm*
Mean Size(Intensity): *779.33 nm* ***Average count rate:*** *2225 kcps*

Detected size(s)

Size (nm)	Intensity	Decay Rate.	Diffusion Coeff. (m²/s)
115.3	0.15	3598.62	69.00972E-013
912.88	0.8	454.53	87.16358E-014

Pade Laplace *Acquisition: Continuous (Number) 00:01:59 24.99 °C*



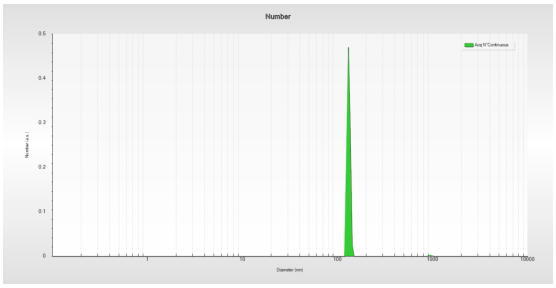
Dispersion statistics

Dn 10%: *112.77 nm* ***Dn 50%:*** *112.77 nm* ***Dn 90%:*** *112.77 nm*
Mean Size(Number): *116.29 nm*

Detected size(s)

Size (nm)	Number	Decay Rate.	Diffusion Coeff. (m²/s)
115.3	1	3598.62	69.00972E-013

SBL *Acquisition: Continuous (Number) 00:01:59 24.99 °C*



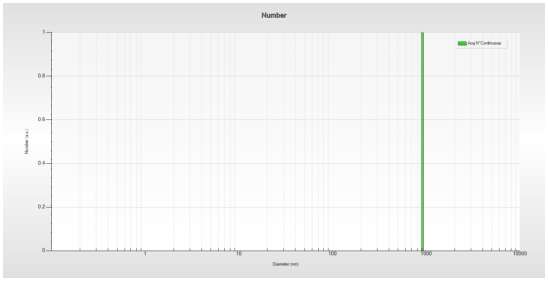
Distribution statistics

Dn 10%: *123.7 nm* ***Dn 50%:*** *129.55 nm* ***Dn 90%:*** *135.68 nm*
Mean Size(Number): *135.17 nm*
Solution index: *15*

Peak *: 1* ***Mode:*** *129.55 nm* ***Mean:*** *130.37 nm* ***Std Dev:*** *5.2 %* ***Intensity:*** *100 %*

Fig. S14 DLS analysis of p-MB@ST^{c} in methanol.

Pade Laplace *Acquisition: Continuous (Number) 00:01:29 24.99 °C*



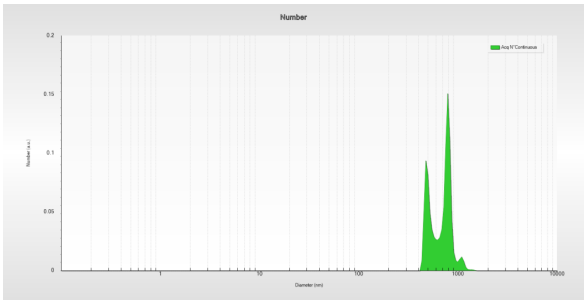
Dispersion statistics

Dn 10%: 903.28 nm **Dn 50%:** 903.28 nm **Dn 90%:** 903.28 nm
Mean Size(Number): 903.28 nm

Detected size(s)

Size (nm)	Number	Decay Rate.	Diffusion Coeff. (m²/s)
917.81	1	452.09	86.69613E-014

SBL *Acquisition: Continuous (Number) 00:01:29 24.99 °C*



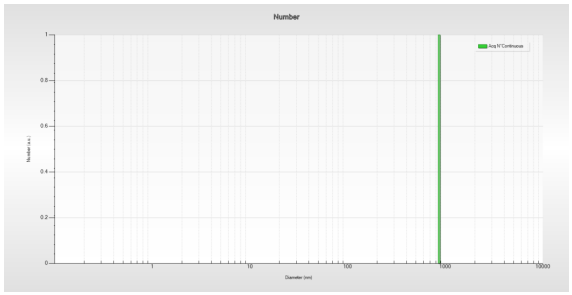
Distribution statistics

Dn 10%: 472.82 nm **Dn 50%:** 716.84 nm **Dn 90%:** 862.47 nm
Mean Size(Number): 685.62 nm
Solution index: 4

Peak :1 **Mode:** 786.29 nm **Mean:** 775.49 nm **Std Dev:** 9.86 % **Intensity:** 56.86 %
Peak :2 **Mode:** 472.82 nm **Mean:** 510.66 nm **Std Dev:** 10.47 % **Intensity:** 38.78 %
Peak :3 **Mode:** 1086.79 nm **Mean:** 1102.46 nm **Std Dev:** 9.42 % **Intensity:** 4.36 %

Fig. S15 DLS analysis of p,o-[0.01MB/Ph]@ST-H in methanol.

Pade Laplace *Acquisition: Continuous (Number) 00:02:58 24.99 °C*



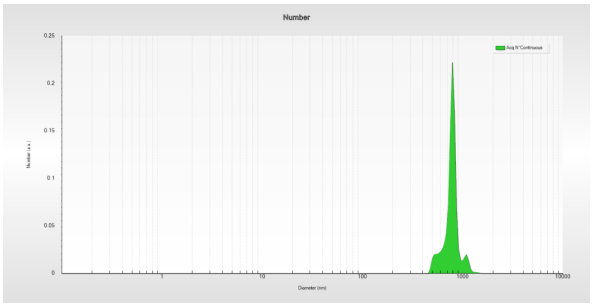
Dispersion statistics

Dn 10%: 862.47 nm **Dn 50%:** 862.47 nm **Dn 90%:** 862.47 nm
Mean Size(Number): 862.47 nm

Detected size(s)

Size (nm)	Number	Decay Rate.	Diffusion Coeff. (m²/s)
846.23	1	490.33	94.02945E-014

SBL *Acquisition: Continuous (Number) 00:02:58 24.99 °C*



Distribution statistics

Dn 10%: 595.8 nm **Dn 50%:** 786.29 nm **Dn 90%:** 903.28 nm
Mean Size(Number): 777.71 nm
Solution index: 4

Peak :1 **Mode:** 786.29 nm **Mean:** 756.47 nm **Std Dev:** 13.78 % **Intensity:** 92.65 %
Peak :2 **Mode:** 1086.79 nm **Mean:** 1095.39 nm **Std Dev:** 8.63 % **Intensity:** 7.35 %

Fig. S16 DLS analysis of o-Ph@ST-H in methanol.

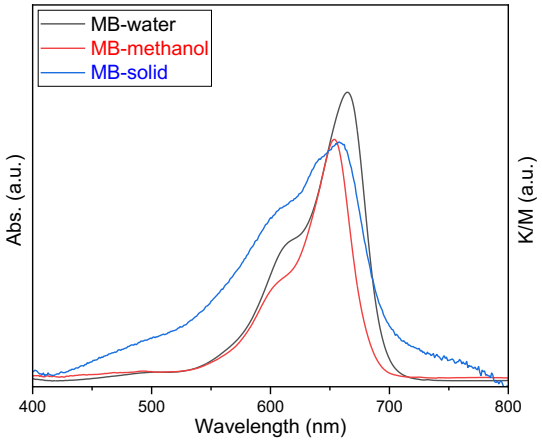


Fig. S17 UV-visible spectra of methylene blue in aqueous solution (black line), in methanol (blue line) and in solid state (red line).

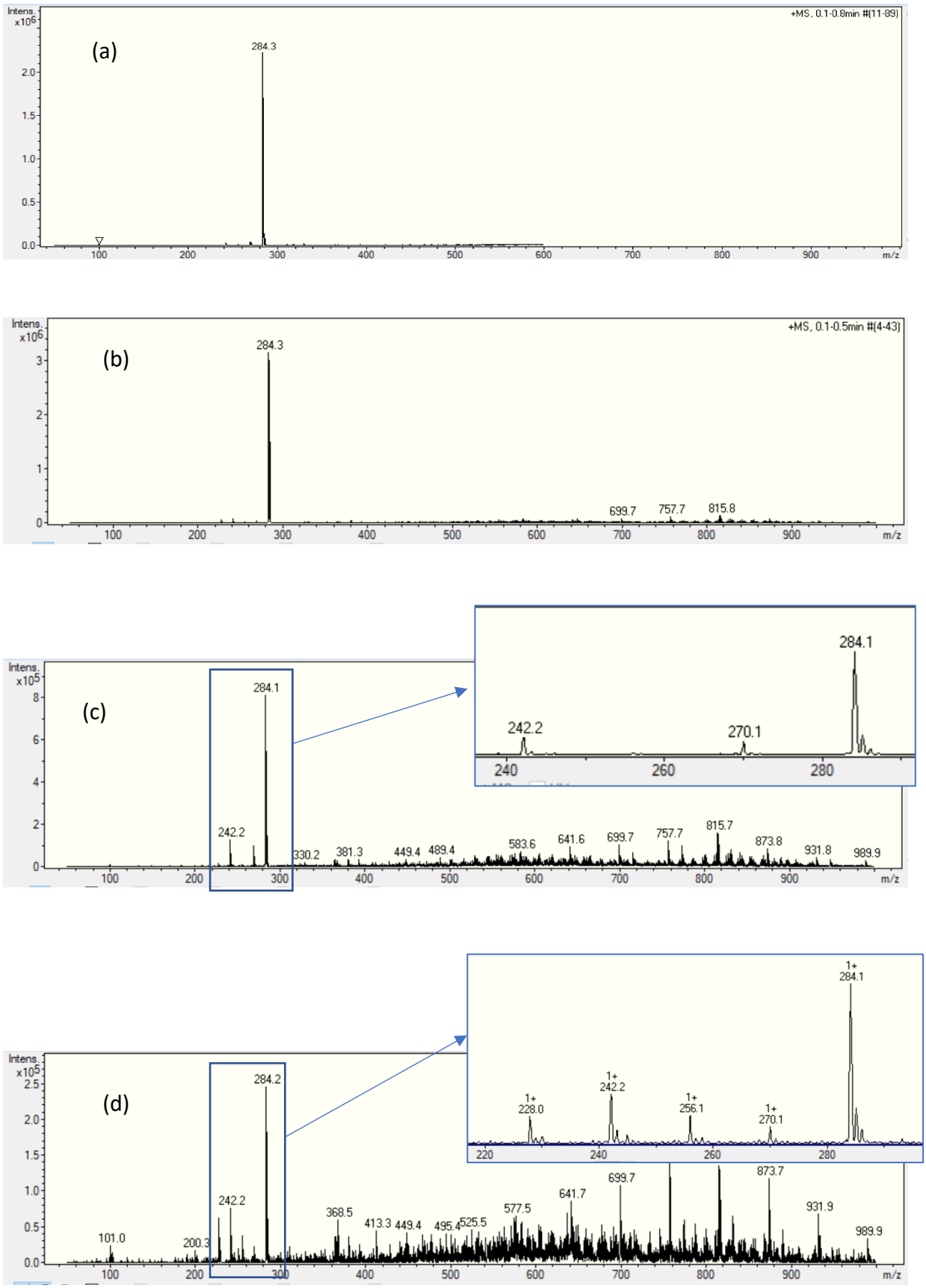


Fig. S18 ESI-MS spectra registered in methanol solution for (a) bare MB, (b) o-[0.01MB/Ph]@ST-H, (c) p,o-[0.01MB/Ph]@ST-H and (d) p-MB @ST^{c}.

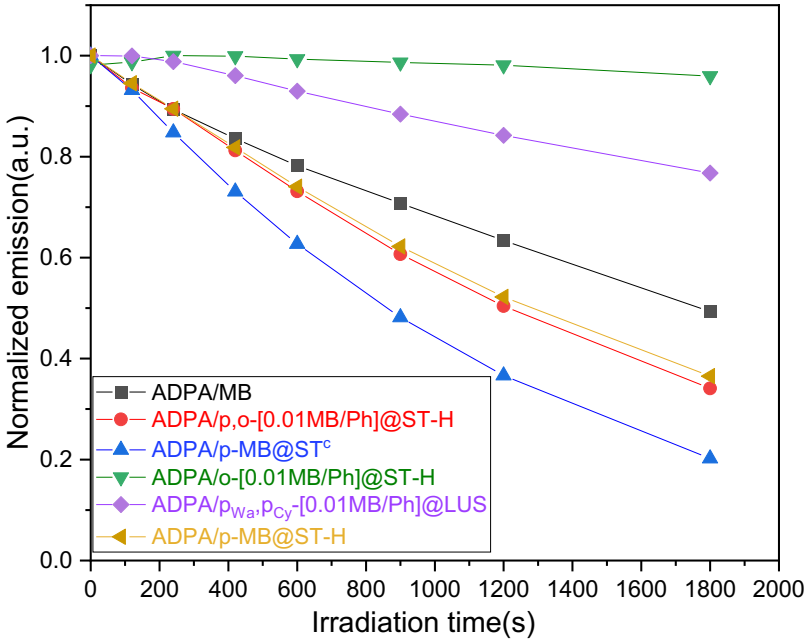


Fig. S19 Time following of the ADPA luminescence (λ_{em} = 409 nm) decay as a function of irradiation time of different MB-containing samples, λ_{ex} = 358 nm in MeOH.

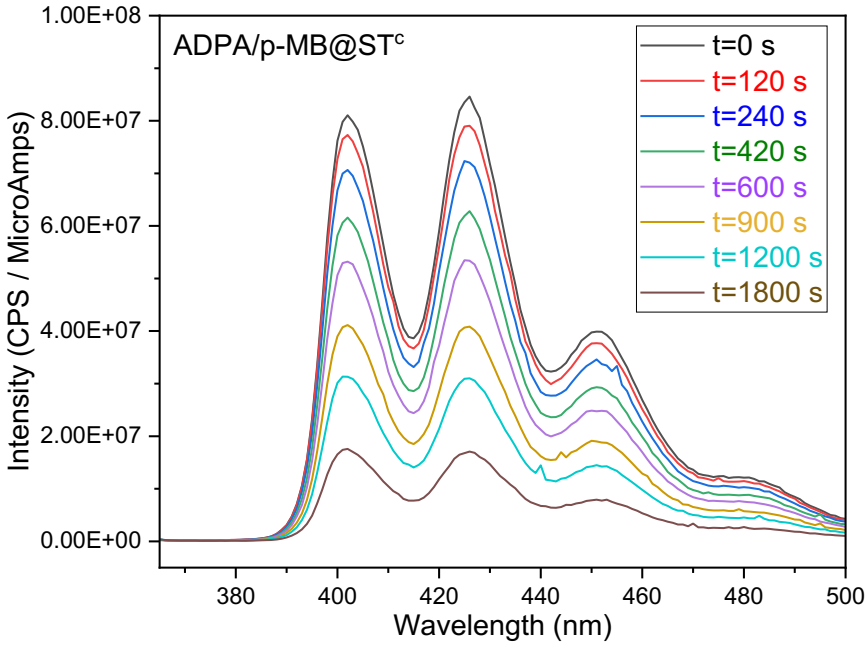


Fig. S20 Emission spectra for ADPA/p-MB@ST^c sample after different irradiation times λ_{ex} = 358 nm, solvent = MeOH.

Tables

Table S1. ICP and TGA analyses of selected samples

sample	ICP	TGA					
	% of C	% loss 200 °C	% C (MB)	% loss 600 °C	% C (Ph)	% of MB^+Cl^+ trihydrate vs. Si_{inorg} [(b)]	% of Ph-SiH_3 vs. Si_{inorg}
o-Ph@ST-H	6.67			7.25	6.78		11.40
o-[0.01MB/Ph]@ST-H	1.47	2.09	1.41			2.75	
p-MB@ST^c	0.83	1.2[(a)]	0.81			1.58	
p,o-[0.01MB/Ph]@ST-H	6.76	0.8[(a)]	0.54	7.31	6.83	1.05	11.41

(a) estimated value from TGA curve; (b) Si_{inorg} corresponds to silicon from the matrix, in contrast to Si_{org} that is the silicon apported by the organosilane, here the phenylsilane

Comments on Table S1

For o-Ph@ST-H, the amount of carbon found by ICP (6.67%) is very close to that calculated from TGA (6.77%), and corresponds exclusively to silane-attached phenyl functions (overall, as inferred from TGA, 11.4% in weight of Ph-silane is present in the final inorganic silica matrix). As expected, a slightly higher carbon content (6.76%) was found by ICP for o,p-[0.01MB/Ph]@ST-H, where o-Ph@ST-H nanoparticles were used as support to attach MB in a post-synthesis procedure. The additional carbon content comes presumably from the grafted MB, though the low 0.09% difference precludes a precise quantification in this case. TGA analysis of p,o-[0.01MB/Ph]@ST-H sample yielded a somewhat higher overall carbon content (7.37%) but still of the same order of magnitude.

Concerning the p-MB@ST^c sample, where calcination was carried out before the incorporation of MB, a much lower carbon percent of 0.83% was measured in ICP. This value is in good agreement with that calculated from TGA (0.81%) and certainly corresponds to MB. Finally, the one-pot o-[0.01MB/Ph]@ST-H sample presents a completely unexpected behaviour since no significant amounts of Ph functions were found at 600 °C in TGA analysis (see main text), whereas a mass loss of 2.09 % is observed around 200 °C. Assuming that this mass loss corresponds to MB^+ cations, the calculated carbon percent is 1.41%, which is consistent with the 1.47% found in ICP.

Table S2. Porous volume deduced for the N_2 sorption isotherms at p/p° = 0.9 ($g.mL^{-1}$)

ST-H	1.4
ST^c	1.2
o-Ph@ST-H	2.1
o-[0.01MB/Ph]@ST-H	2.1
p-MB@ST^c	1.3
p,o-[0.01MB/Ph]@ST-H	1.9