Rapid Fabrication And High-resolution 3D Printing Of Photopolymer/MOFs Composites With Superior Selective Absorption of Cationic dye

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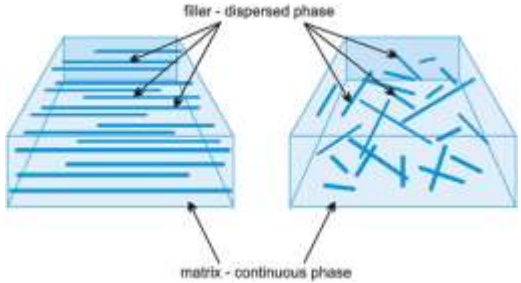
Background

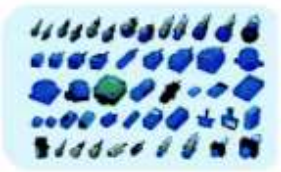


Composites = Matrix + filler(s)

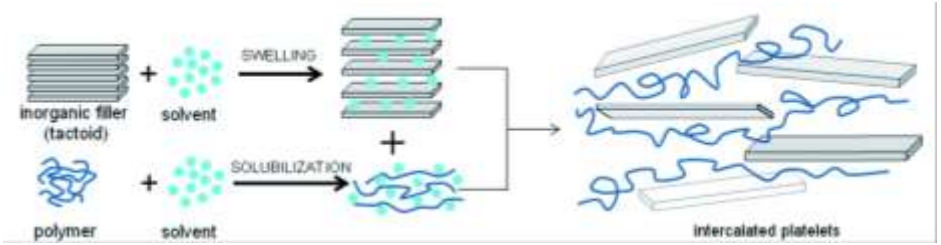
Aerospace

Civil engineering

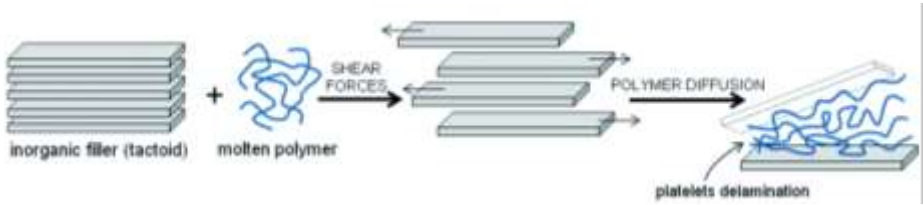
Electronics



Sensors



Solution casting

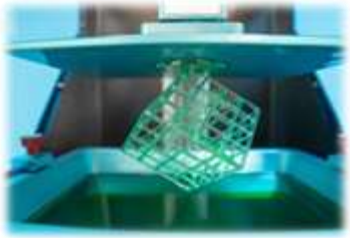


Melt blending

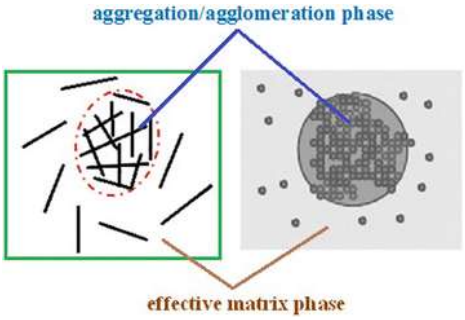
Photopolymerization technique

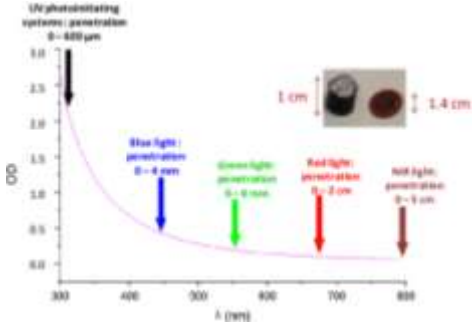
Photoinitiating systems (PIs):

- Photoinitiators
- Co-initiators/ additives



Some concerns….





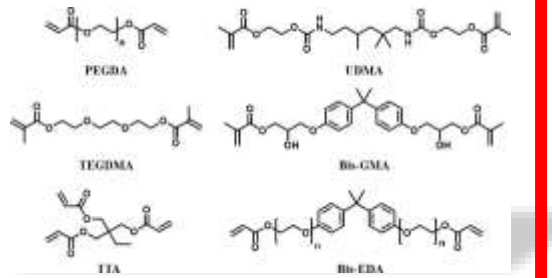
- Aggregation
- High loading of fillers is hard to achieve
- Hard to prepare thick sample due to light penetration

ACS Nano, 2018, 12, 9, 9040–9050;
Eur. Polym. J.. 2018; 98:430-8; Catalysts, 2020, 10(9), 953

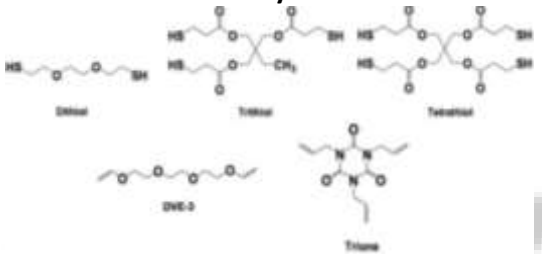
ACS Appl. Polym. Mater. 2019, 1, 4, 593–611

Selections of monomers/fillers

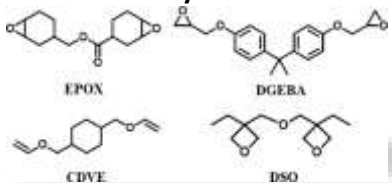
(Meth)acrylate-Based Photocurable Systems

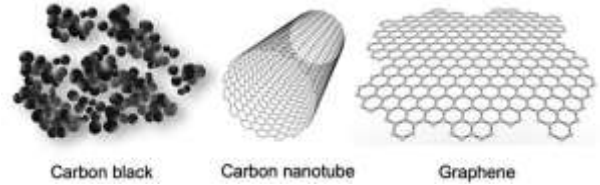


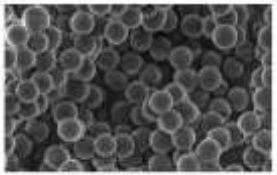
Thiol-ene Systems



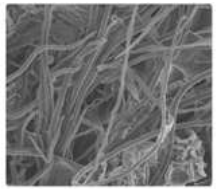
Cationic Systems



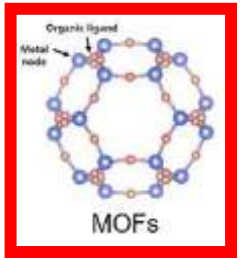




Silica-based

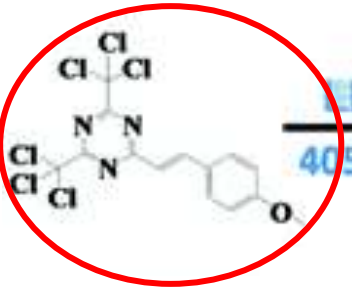


Cellulose fibers



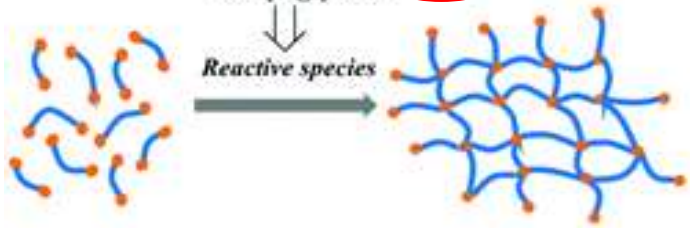
ACS Appl. Polym. Mater., 2019, 1, 4, 593–611;
ACS Appl. Mater. Interfaces, 2021, 13, 38, 46033–46042

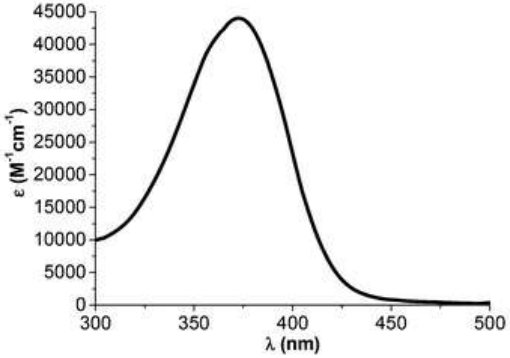
Investigated photoinitiator



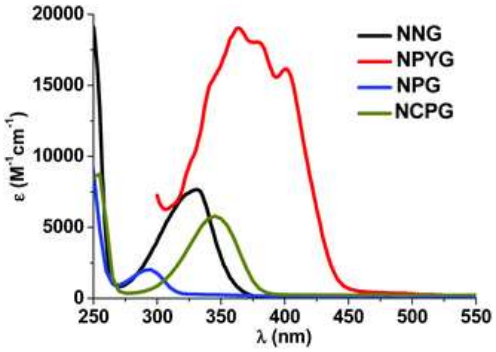
2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (**triazine**)

N-(1-pyrenyl)glycine (**NPYG**)



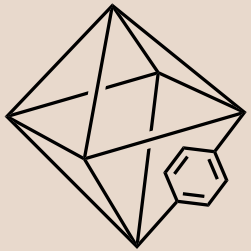
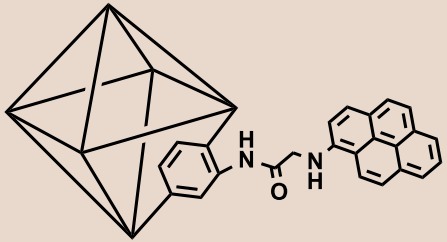
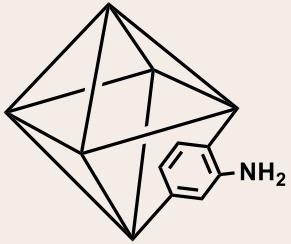
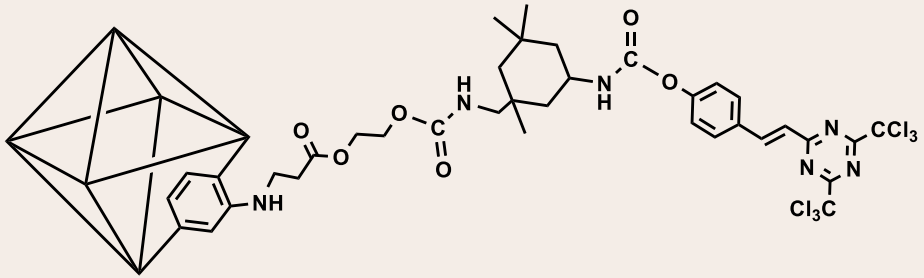


- Type I photoinitator
- UV absorption up to 470 nm
- High molar extinction coefficient at visible light region

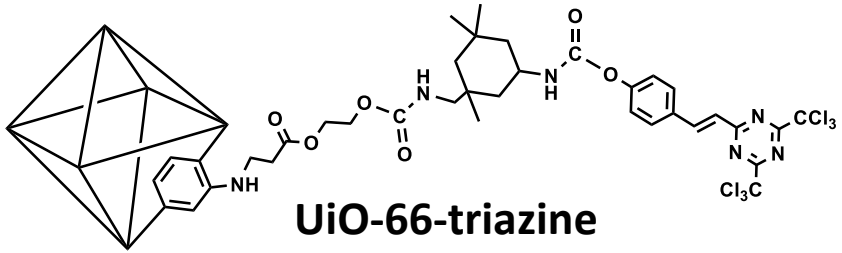


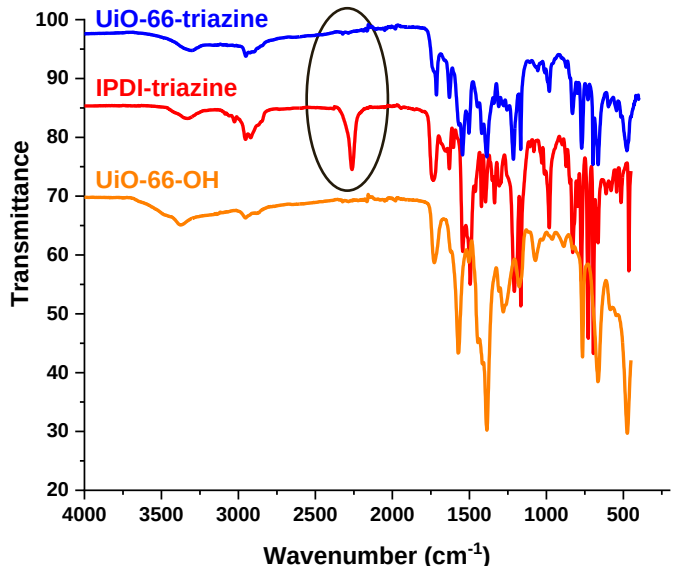
Polym. Chem., 2014, 5(20), pp.6019-6026;
Macromol. Chem. Phys., 220(18), p.1900315

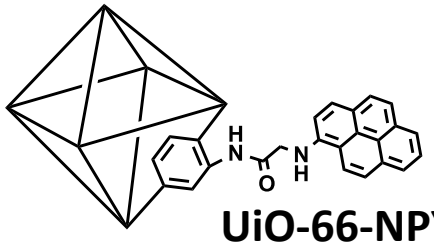
Synthesis route of various MOFs

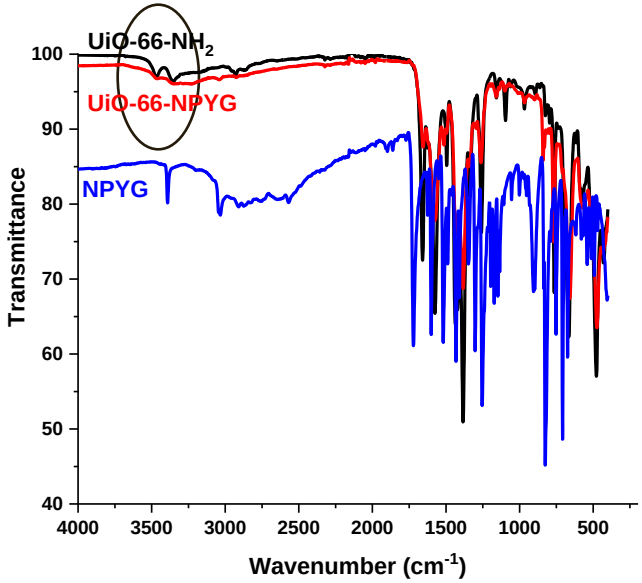
Unmodified MOFs	Photoinitiator-grafted MOFs
 UiO-66	 UiO-66-NPYG
 UiO-66-NH_2	 UiO-66-triazine

Fourier transform infrared (FTIR)

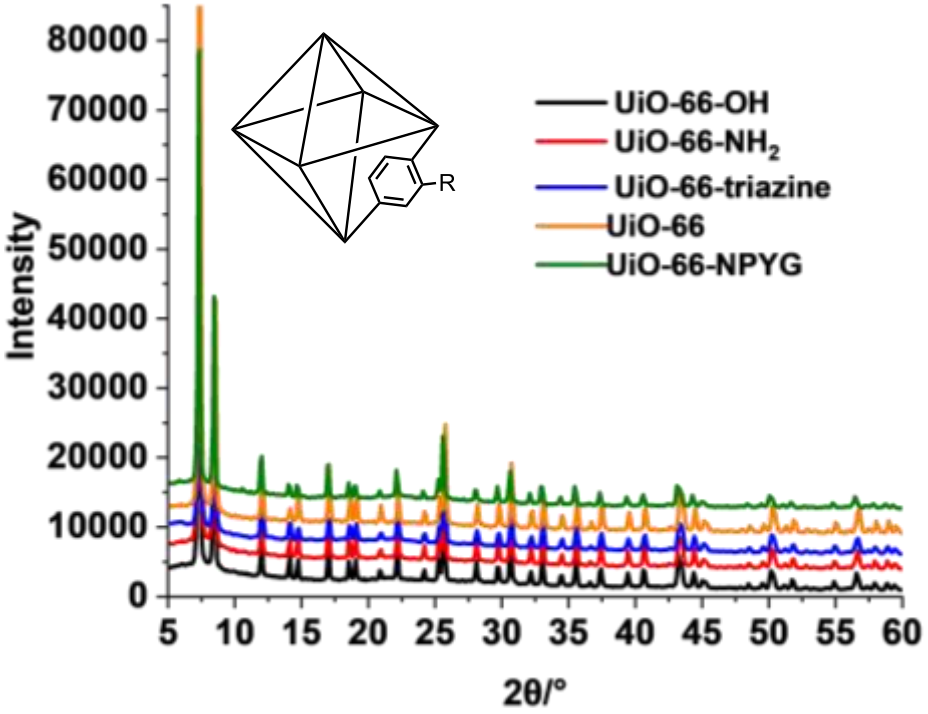


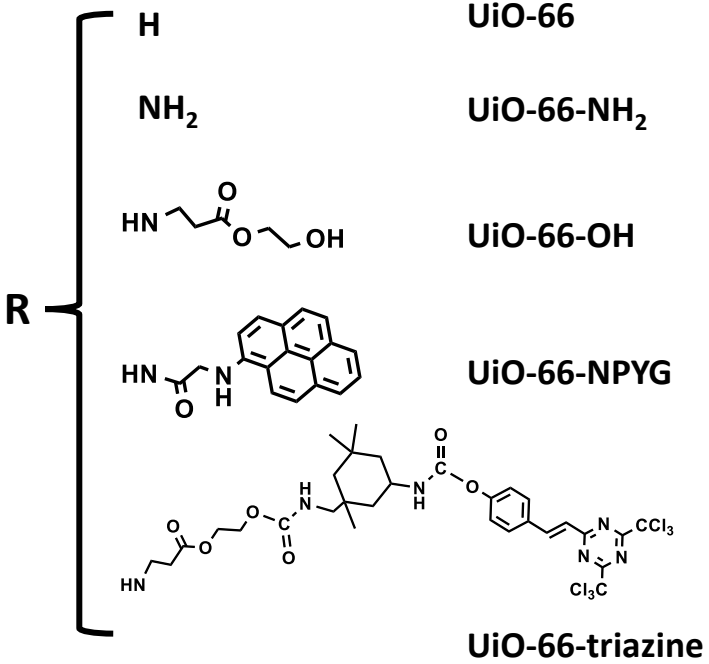






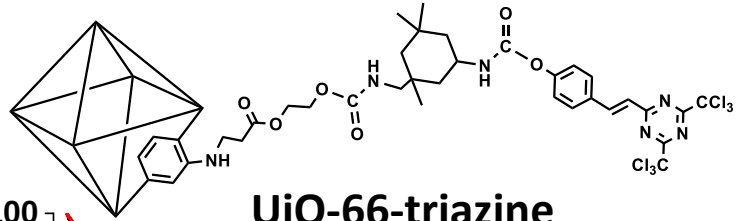
X-Ray Diffraction(XRD)

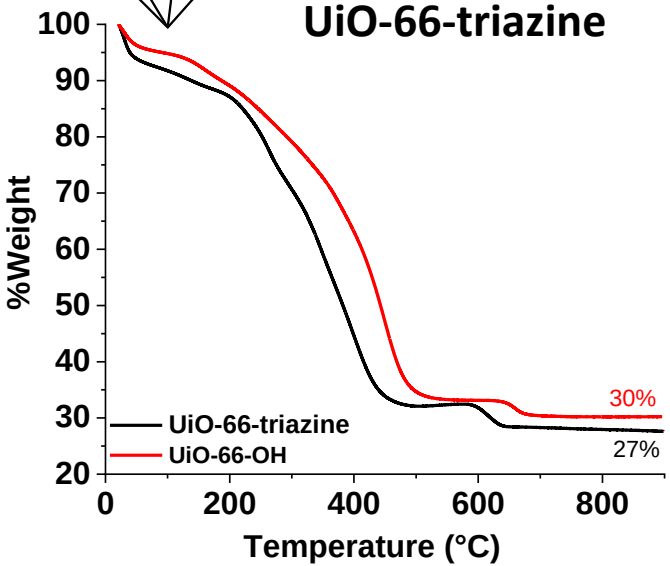




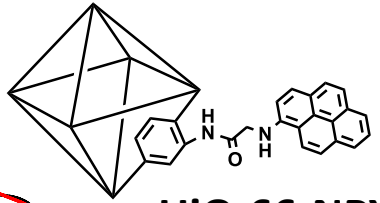
Modified MOFs retain their crystal structure after several rounds of reaction

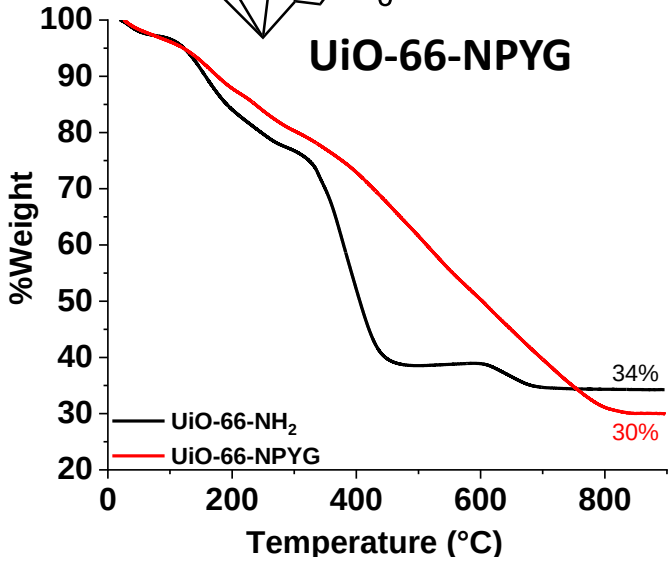
Thermogravimetric analysis(TGA)





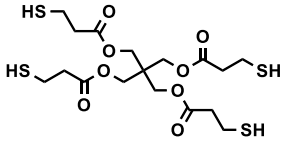
% of triazine linked to the UiO-66-NH_2: 3 wt.%





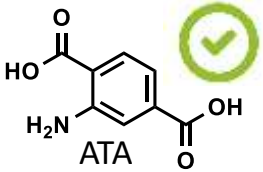
% of NPYG linked to the UiO-66-NH_2: 4 wt.%

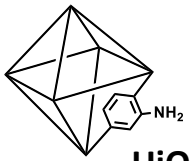
Photopolymerization profile



Tetrathiol

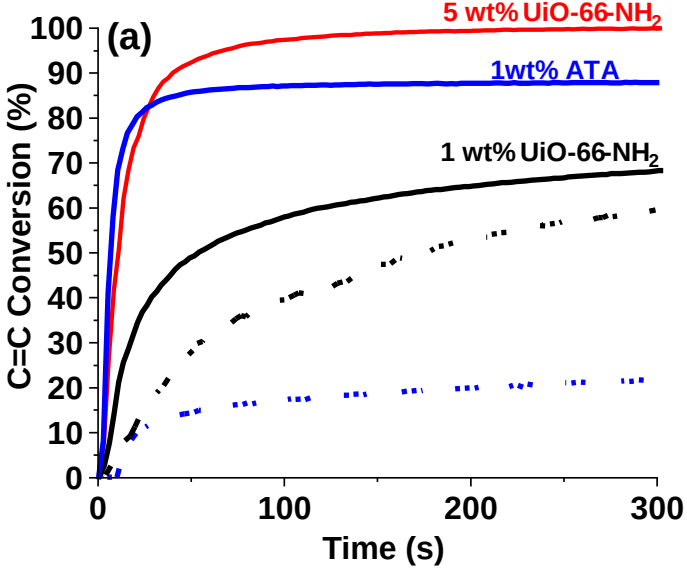
DVE-3

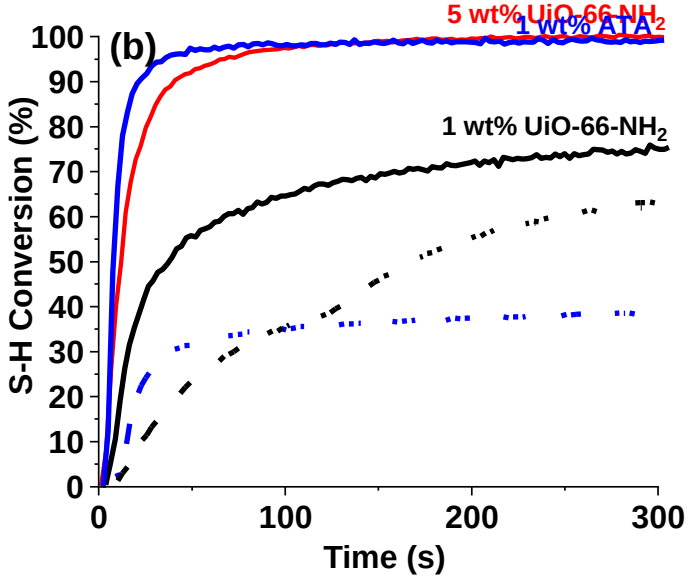




$UiO\text{-}66\text{-}NH_2$

UiO-66

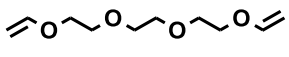




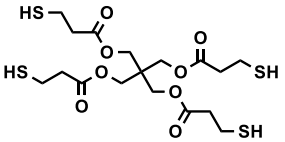
Polymerization with LED@410 nm

The photoinitiation ability of ATA is significantly supressed by oxygen inhibition

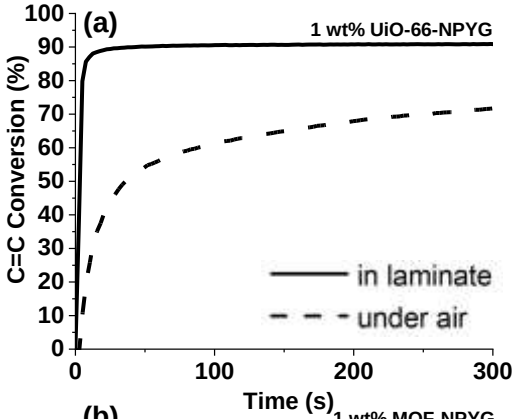
Photopolymerization profile

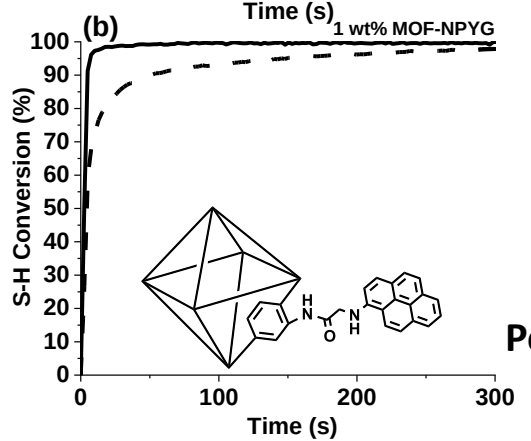


DVE-3



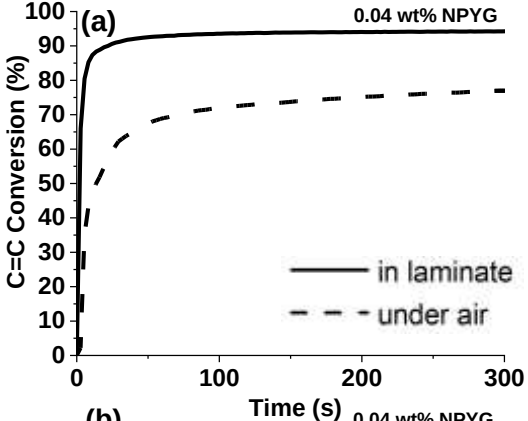
Tetrathiol

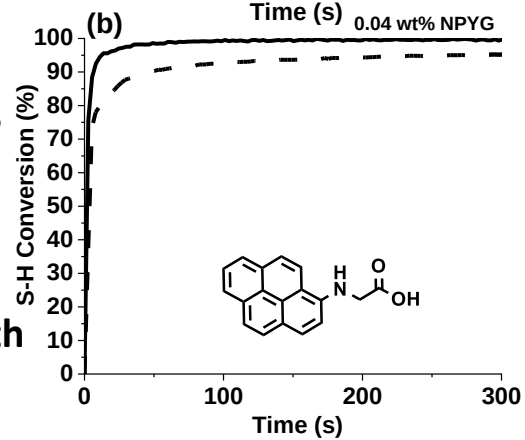




Polymerization with

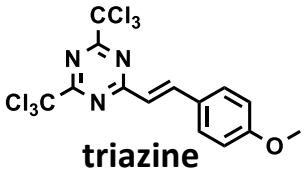
LED@410 nm

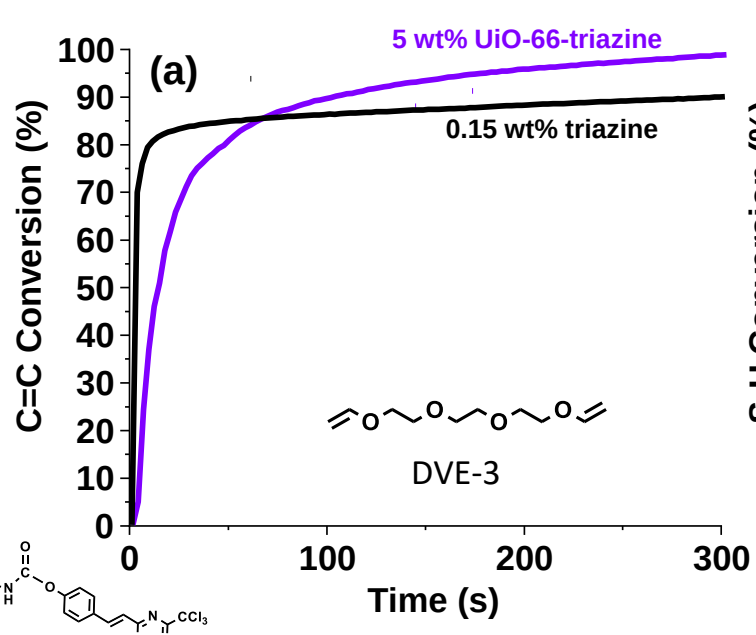


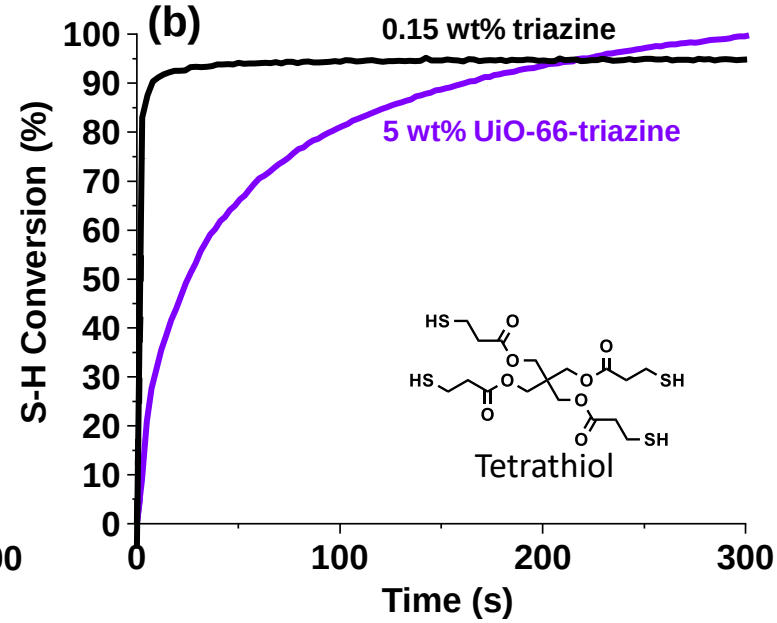


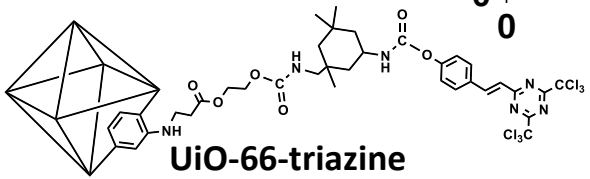
UiO-66-NPYG shows almost the same efficient as the free NPYG (**same** molar concentration of NPYG)

Photopolymerization profile





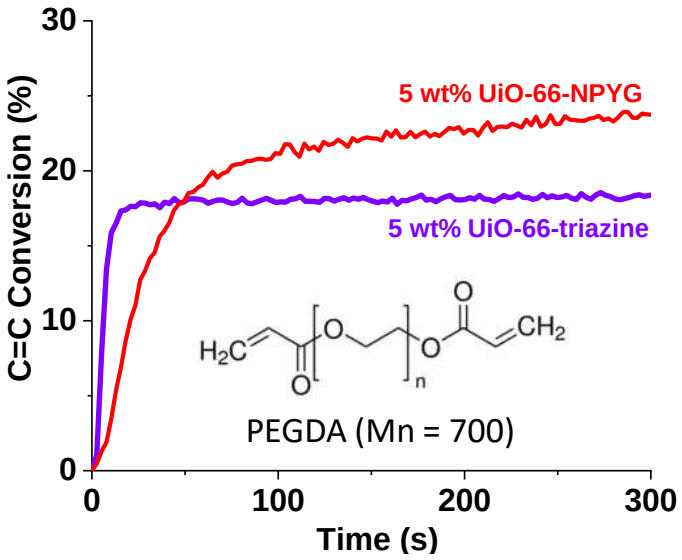


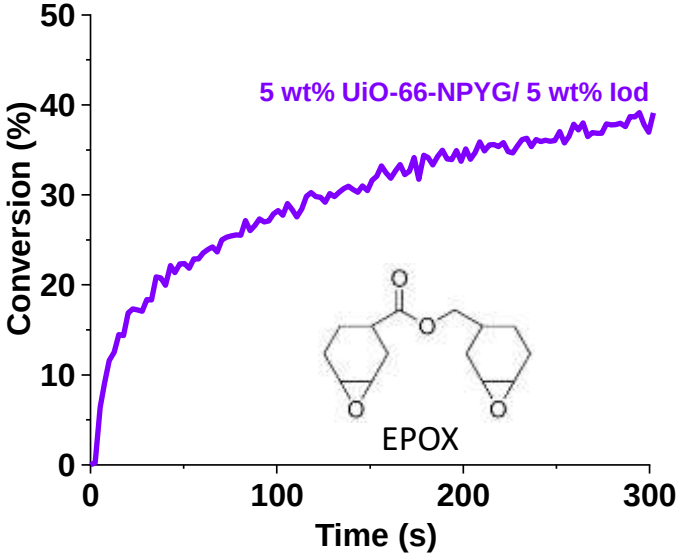


Polymerization with LED@410 nm

UiO-66-triazine shows similar efficient as free triazine (**same** molar concentration of triazine)

Versatilities of photoinitiator-grafted MOFs

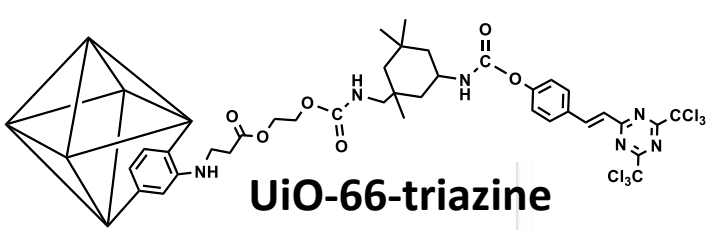




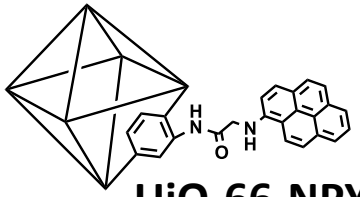
Polymerization with LED@410 nm

UiO-66-NPYG able to initiate thiol-ene, free radical and cationic system.

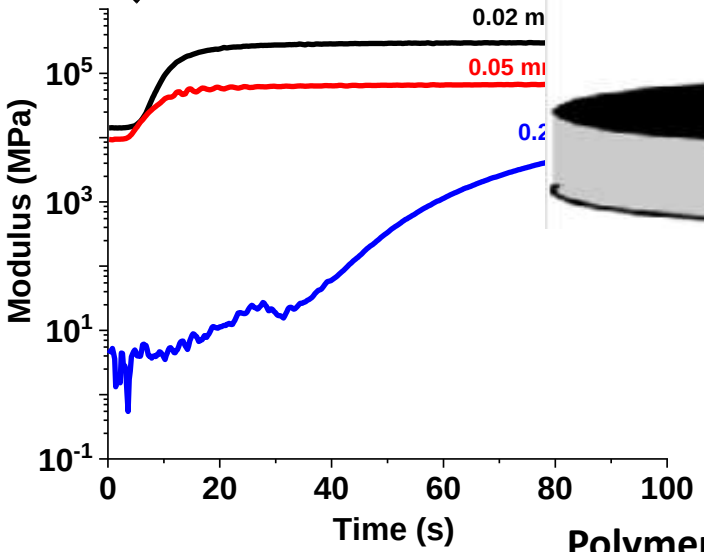
Thick curing – photorheometer

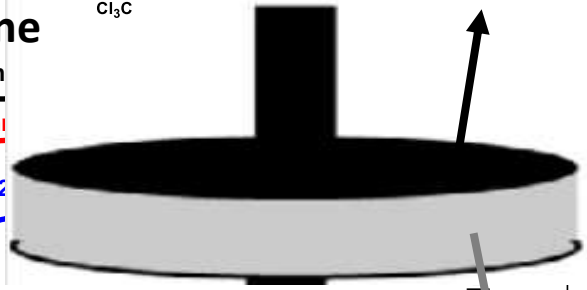


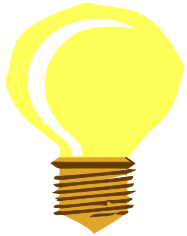
UiO-66-triazine

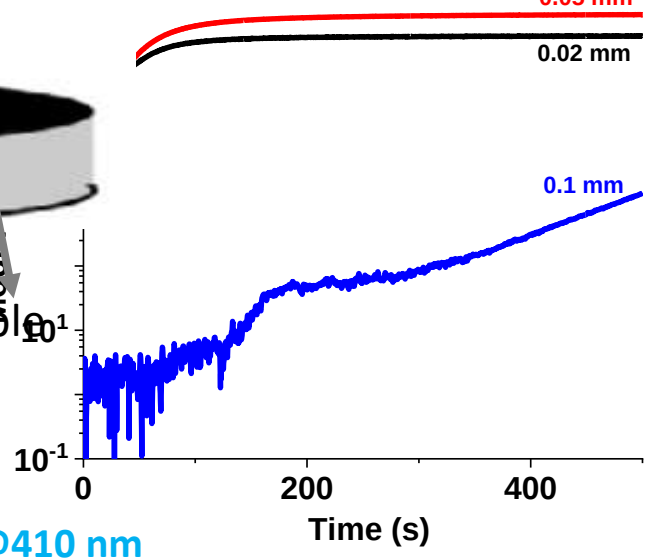


UiO-66-NPYG





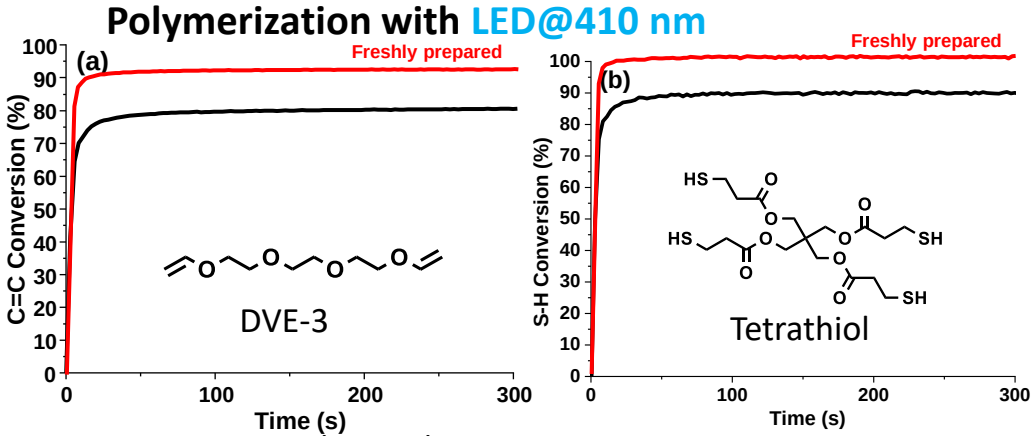




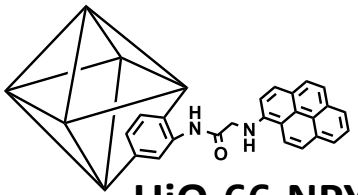
Polymerization with LED@410 nm

Polymerize well in thicker samples→ the delay between samples with different curing thickness is negligible

Storage stability

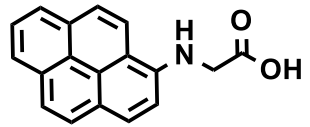


1 wt% UiO-66-NPYG/DVE-3/tetrathiol after storage for 7 days



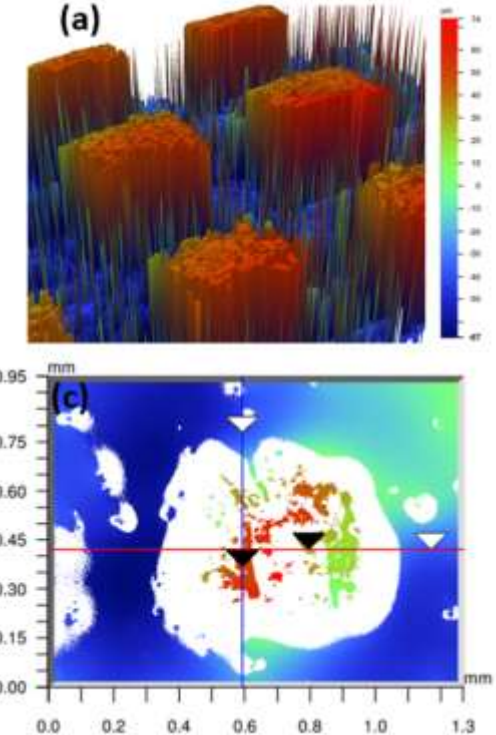
UiO-66-NPYG

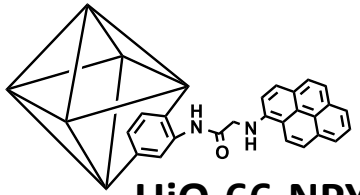
UiO-66-NPYG can stabilize reactive thiol-ene system and extend storage shelf life → Only after two weeks, it became a sticky gel



0.04 wt% NPYG/DVE-3/tetrathiol after storage for 3 days → polymerized

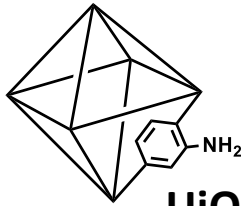
High Resolution Direct Laser Writing





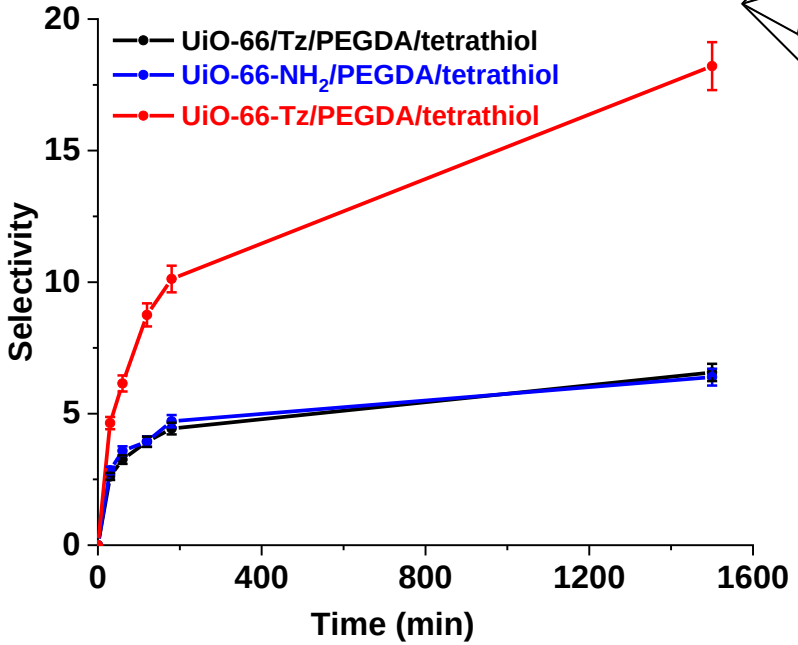
UiO-66-NPYG

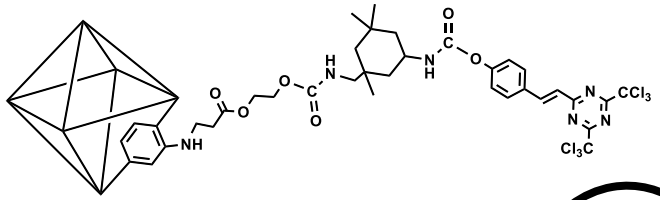
VS



UiO-66-NH_2

Selective dye absorption



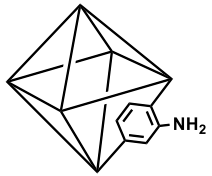


UiO-66-triazine

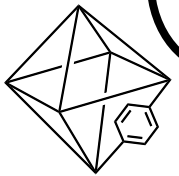
?

Methylene blue

Methyl orange



UiO-66-NH_2



UiO-66

Conclusions

- Successful development of two dual-functional violet-light-sensitive photoinitiator-grafted MOFs (UiO-66-triazine and UiO-66-NPYG) which act as both photoinitiator and fillers.

- Modified MOFs show versatilities in initiating various system including thiol-ene, free radical and cationic.

- Modified MOFs show abilities on thick curing. Specifically, UiO-66-NPYG exhibits excellent phtoinitiation ability and storage stability even in reactive thiol-ene system, allowing application in high resolution direct laser writing

- UiO-66-Tz/PEGDA/tetrathiol polymer composite exhibiting approximately 3 times greater selectivity towards the cationic dye compared to other investigated MOF/polymer composites.

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Prof. Yun Liu

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RSC

Thanks for your attention!

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