SUPPORTING INFORMATION

MOF-Based Polymeric Nanocomposite Films as Potential Materials for Drug Delivery Devices in Ocular Therapeutics

J. Gandara-Loe,[1] B.E. Souza,[2] A. Missyul,[3] G. Giraldo,[4] J.-C. Tan,[2] J. Silvestre Albero[1,*]

[1]Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-IUMA, Universidad de Alicante, E-03690 San Vicente del Raspeig, Spain

[2]Multifunctional Materials & Composites (MMC) Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK

[3] CELLS-ALBA Synchrotron, E-08290, Cerdanyola del Vallés, Spain

[4] Clínica Clofan, Carrera 48 # 19 A 40, Medellín, Colombia.

* Email: joaquin.silvestre@ua.es

Table of Contents *Page*

- *Equations applied in this study.*

- 30 wt. % UiO-67 encapsulated in a polymeric (PU) 50 µm film was prepared using the following equation (1):

$$UiO\text{-}67\ wt.\% = \left(\frac{m_{UiO-67}}{m_{UiO-67} + m_{PU}}\right) x\ 100\% \quad (1)$$

where m_{UiO-67} is the weight of UiO-67 nanoparticles dispersed in THF and m_{PU} is the weight of PU pellets dissolved in THF.

- Maximum amount of brimonidine that can be released (2) and real percentage released (3) was calculated using the following equation:

$$m_{bri-max} = \frac{C_0 - C_{eq}}{m_{film}} \quad (2)$$

$$\%\ released = \frac{C_{eq-released} \times v}{m_{bri-max}} \quad (3)$$

where $m_{bri\text{-}max}$ is the maximum amount of brimonidine adsorbed in a given mass of film (m_{film}), C_0 is the initial concentration of brimonidine, C_{eq} is the concentration after the adsorption reached the equilibrium, $C_{eq\text{-}released}$ is the concentration measured after a given time during the releasing process in PBS solution and v the volume of PBS.

- *Tables*

Table S1. Thermogravimetric results of the different samples evaluated.

Sample	1st stage		2nd stage		3rd stage		
	ΔT (ºC)	ΔW (wt.%)	ΔT (ºC)	ΔW (wt.%)	ΔT (ºC)	ΔW (wt.%)	T_m (ºC)
UiO-67	30-200	25.3	200-440	4.7	440-600	31.5	540
PU	30-190	0.4	235-500	94.7	500-600	0.7	337
UiO-67@PU	30-190	2.7	190-370	68.9	455-600	8.4	252

ΔT: temperature range of the thermal decomposition.
ΔW: Total weight loss at the main decomposition process
T_m: The degradation temperature corresponding to the maximum weight loss rate of DTG curve.

- *Figures*

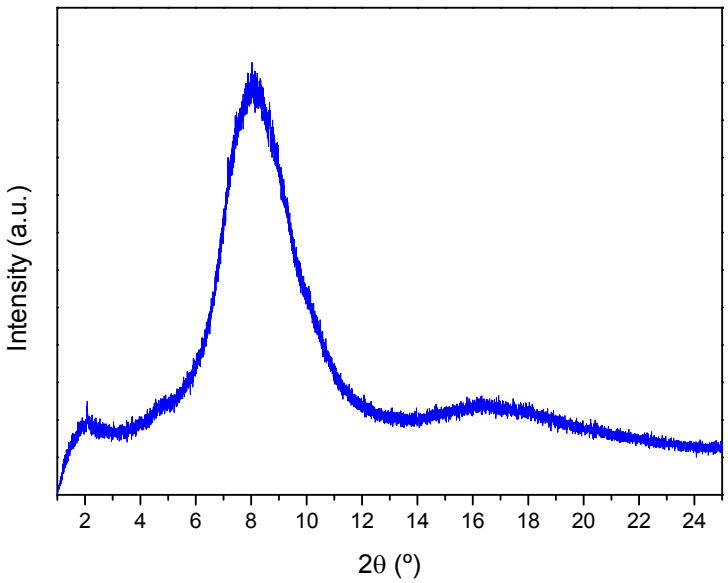

Figure S1. Synchrotron X-ray powder diffraction pattern of pure polyurethane film.

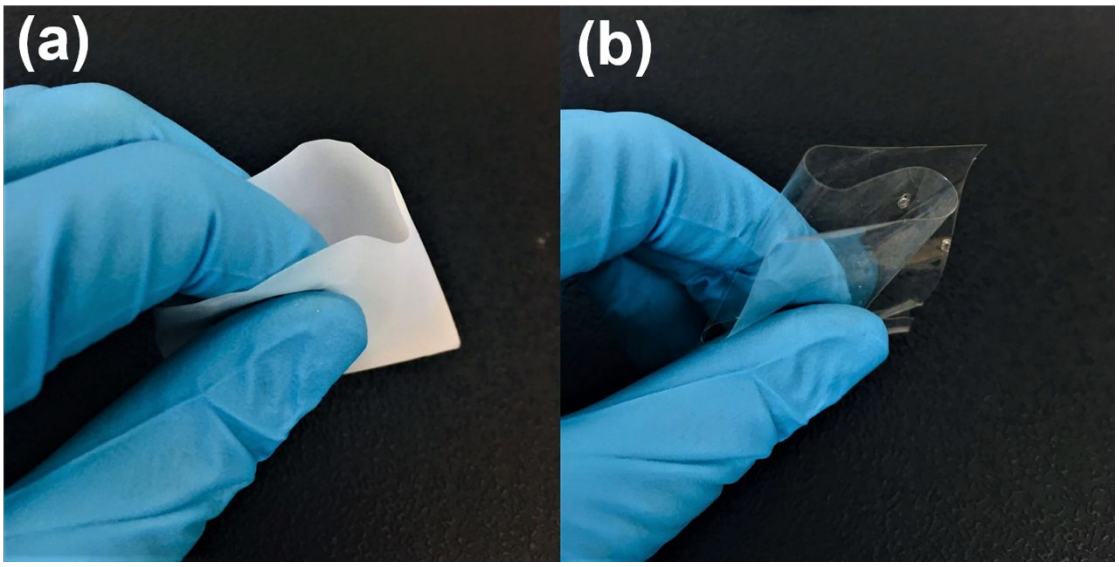

Figure S2. Photographs of the different samples prepared by doctor blading, (a) UiO67@PU and (b) PU films.

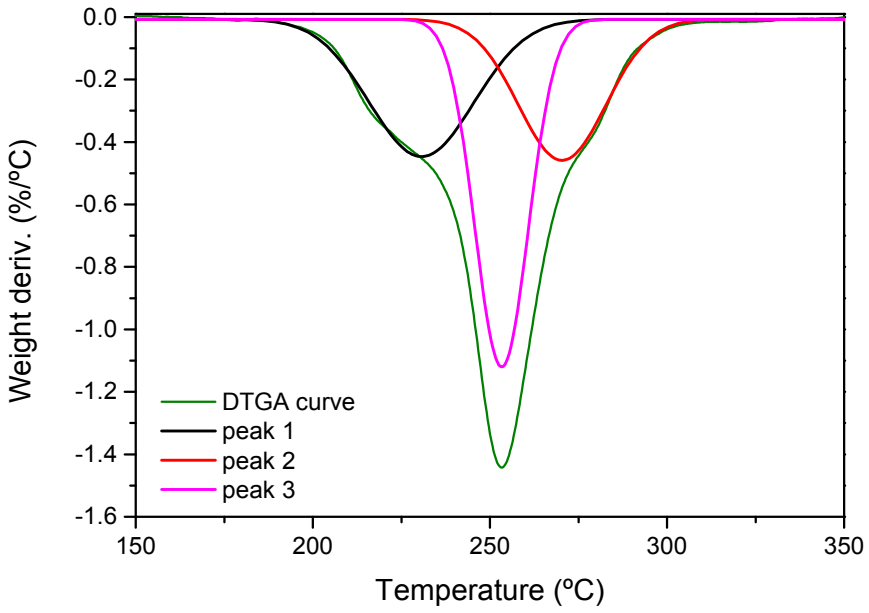

Figure S3. Deconvolution of the DTGA profile for UiO-67@PU film.

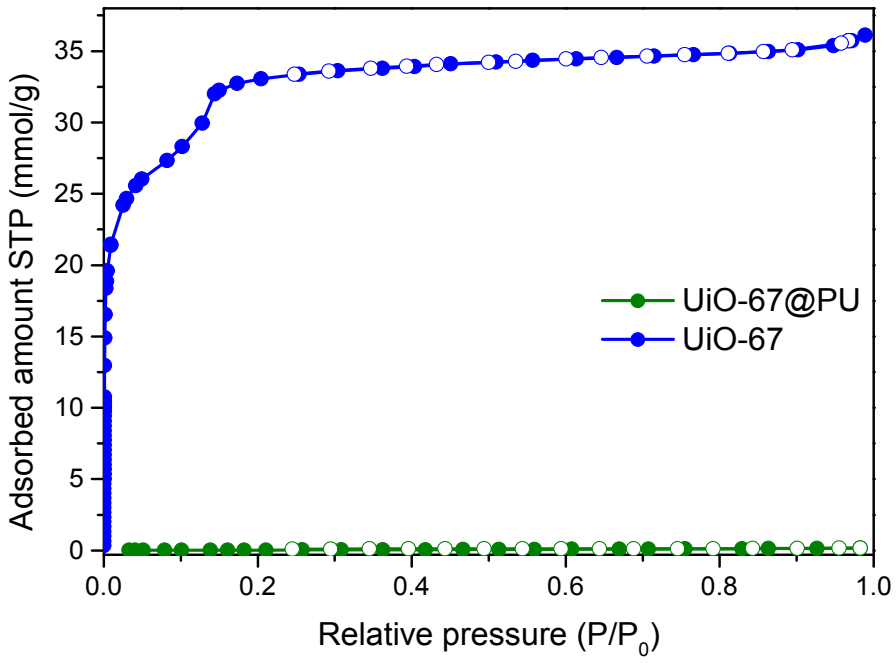

Figure S4. Nitrogen adsorption (filled symbols)-desorption (open symbols) isotherms at -196ºC for UiO-67 and UiO-67@PU film.

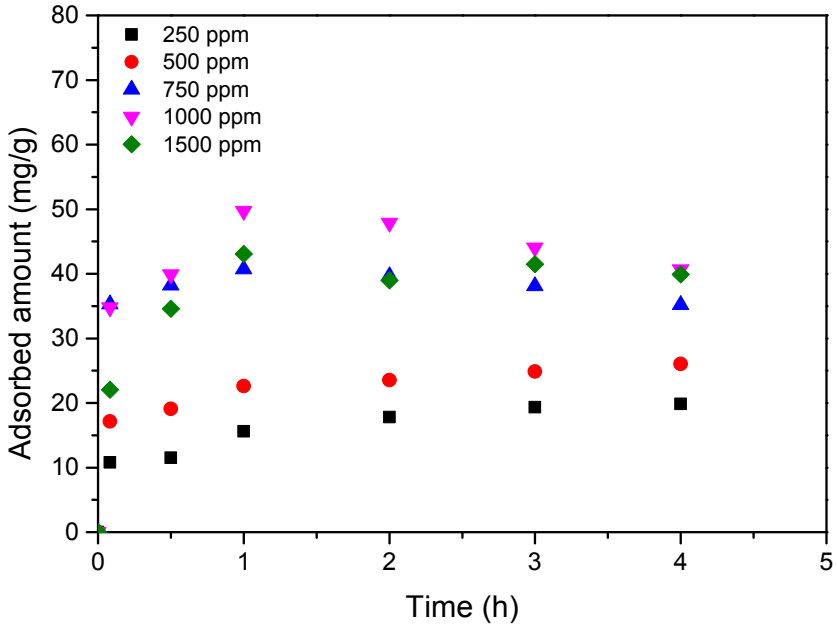

Figure S5. Brimonidine adsorption kinetics in the UiO67@PU film at different initial concentrations.

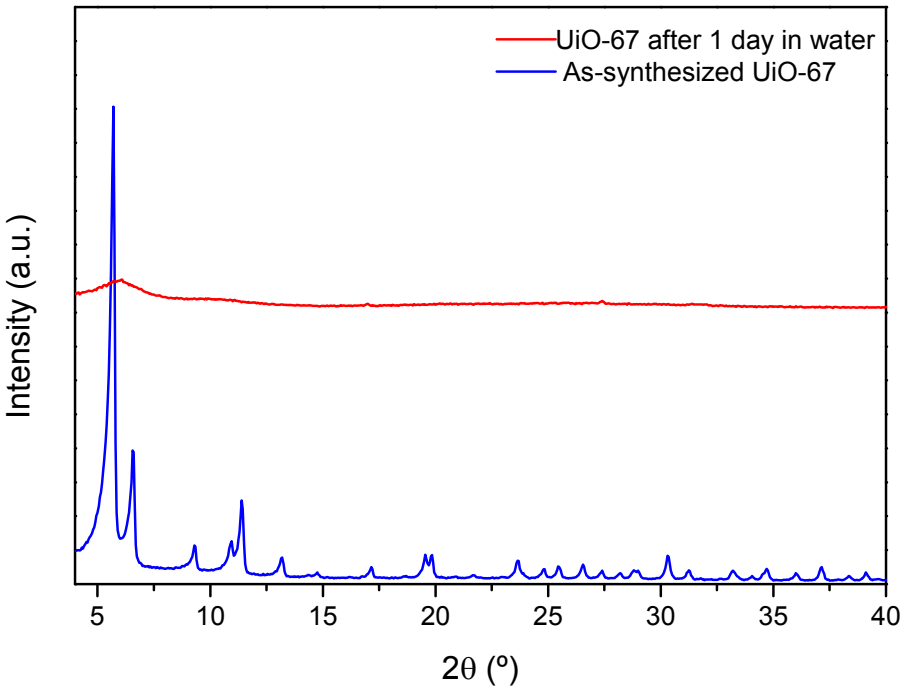

Figure S6. X-ray powder diffraction pattern of as-synthesized UiO-67 and after soaking in water for 1 day.[1]

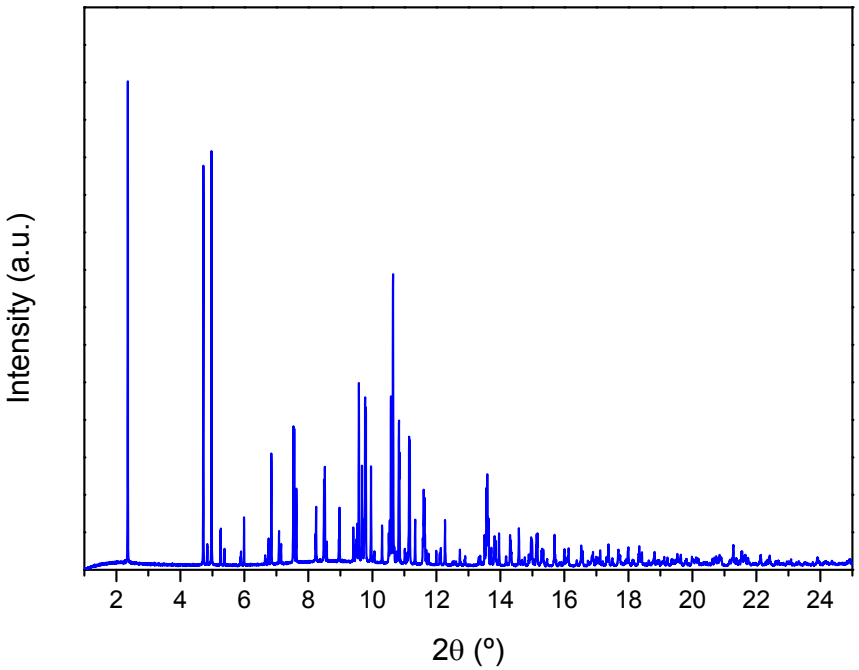

Figure S7. Synchrotron X-ray powder diffraction pattern of brimonidine tartrate.

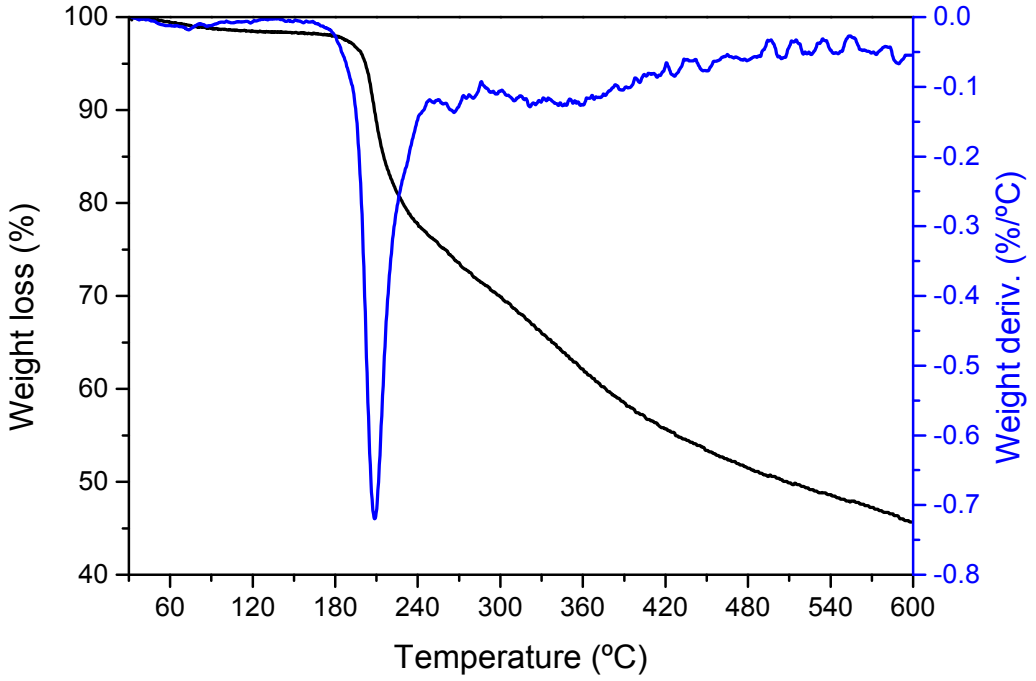

Figure S8. TGA-DTGA profiles for brimonidine tartrate.

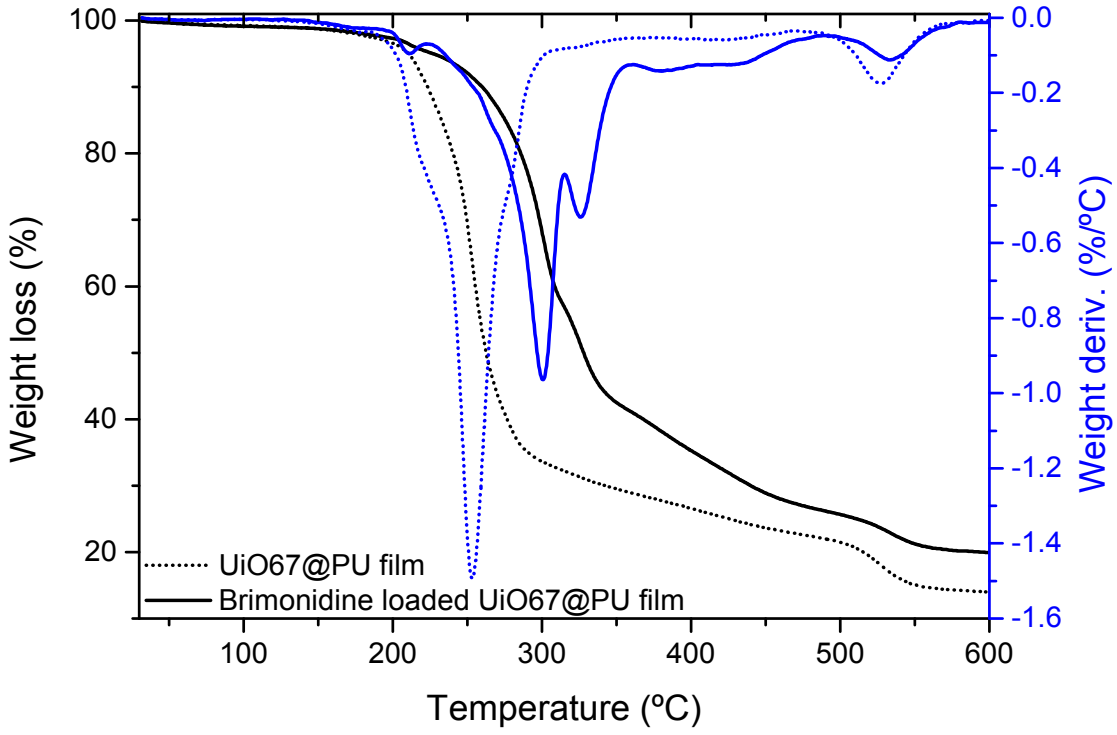

Figure S9. TGA-DTGA profiles for UiO-67@PU film before and after loading with brimonidine.

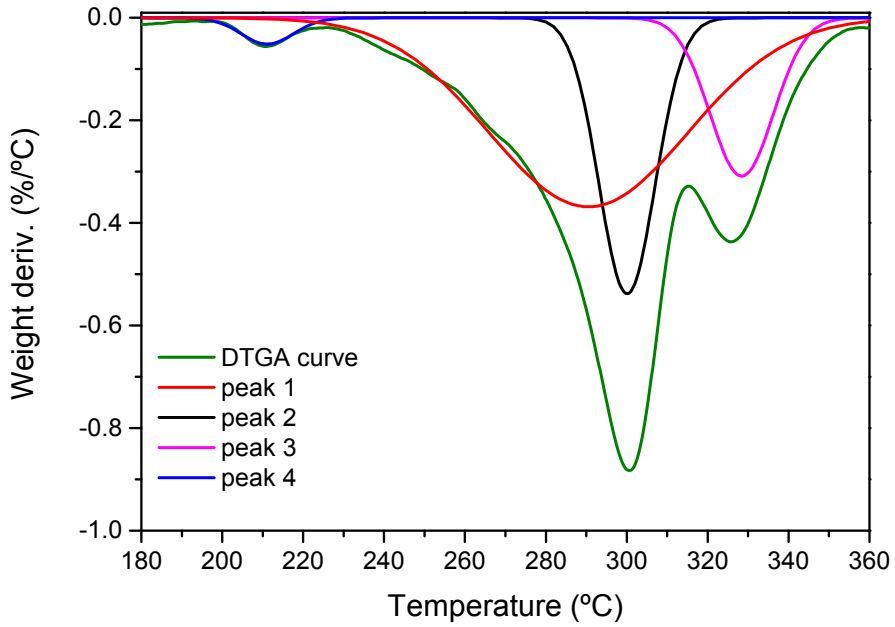

Figure S10. Deconvolution of the DTGA profile in brimonidine loaded UiO-67@PU films.

- *Langmuir model for brimonidine adsorption isotherm.*

Adsorption isotherms are defined as the mathematical relationship between the mass of the adsorbed solute per adsorbent mass unit and the solute concentration remained in the solution when the equilibrium has been reached at constant temperature [2]. The most widely used isotherm models for liquid-solid systems are Langmuir, Freundlich and Prausnitz-Radke [3].

Langmuir model (4) was theoretically developed based on the following assumptions: i) the adsorption occurs in specific sites on the surface of the adsorbent, ii) only one molecule is adsorbed in each active site, iii) there are not interactions between adjacent adsorbed molecules and iv) the adsorption heat is the same for all the active sites. This model is mathematically represented as:

$$q_{eq} = \frac{(C_o - C_{eq}) \cdot v}{m} \qquad (3)$$

$$q_{eq} = \frac{q_{max} \cdot K \cdot C_{eq}}{1 + K \cdot C_{eq}} \qquad (4)$$

Where C_{eq} (mg/L) is the concentration of the solute after the equilibrium has been reached, q_{eq} (mg/g) is the mas of solute adsorbed per unit mass of adsorbent,

q_{max} (mg/g) is the maximum amount of solute that can be adsorbed by the adsorbent, C_o is the initial concentration and K (L/mg) is the Langmuir constant related with the heat of adsorption.

The equation was solved using Statistica 10 software of StatSoft Inc by nonlinear estimation with estimation method of Rosenbrook and Quasi-Newton. The values obtained for brimonidine adsorption in UiO-67@PU nanocomposite films are:

$$q_{max} = 58.44 \pm 1.89 \frac{mg}{g}$$

$$K_{Langmuir} = 2.48 \times 10^{-3}$$

- *Brimonidine chromatograph*

Chromatographic conditions used for the quantification of brimonidine were based in the method developed by Karamanos et al [4]. 10 mM triethylamine 3.2 buffer and acetonitrile were used as mobile phase for the column. Figure S10 shows a typical chromatogram for brimonidine quantified by HPLC.

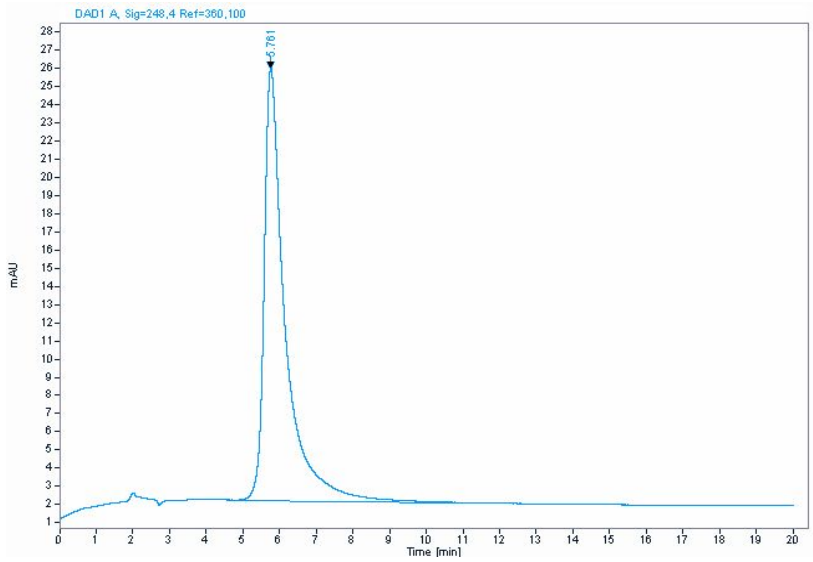

Figure S11. Typical chromatogram for brimonidine using HPLC and detected by UV-Vis.

References

1. Gandara-Loe, J. *et al.* Metal–Organic Frameworks as Drug Delivery Platforms for Ocular Therapeutics. *ACS Appl. Mater. Interfaces* **11**, 1924–1931 (2019).

2. Cooney, D. O. *Adsorption design for wastewater treatment*. (Boca Raton, Fl. : Lewis Publishers, 1999).

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4. Karamanos, N. K., Lamari, F., Katsimpris, J. & Gartaganis, S. Development of an HPLC method for determining the alpha2-adrenergic receptor agonist brimonidine in blood serum and aqueous humor of the eye. *Biomed. Chromatogr.* **13**, 86–88 (1999).