Electronic Supplementary Information

A porous metal–organic framework with a unique hendecahedron-shaped cage: structure and controlled drug release†

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1. Experimental Section

Materials and Physical Techniques

The reagents and solvents were commercially available and were used as received without further purification. IR spectra were recorded in the range of 4000−450 cm^{-1} on a Nicolet 6700 FT-IR spectrometer using the KBr disc technique. Elemental analyses (C, H, N) were performed on a Euro Vector EA3000 CHN elemental analyzer. Thermogravimetric analysis (TGA) for the single phase polycrystalline sample was performed on a SEIKO INSTRUMENTS/EXSTAR TG/DTA 6300 under N_2 atmosphere, in the temperature range of 30−800 °C at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 powder X-ray diffractometer with Cu-Kα_1 radiation (λ = 1.5406 Å). Raman spectrum was measured by Lab RAM HR800 Laser Confocal Micro-Raman Spectroscopy, and the laser wavelength was set at 532 nm. Nitrogen (N_2) adsorption measurement was performed on a Micromeritics ASAP 2020 surface area analyzer at 77 K. UV data were measured on an Agilent 8453UV-Vis spectrometer.

Syntheses of Compounds 1

$Cu(NO_3)_2 \cdot 3H_2O$ (60 mg, 0.25 mmol), 3,5-di(4-carboxyphenyl) benzoic acid (L) (45 mg, 0.125 mmol) and pyrazine (10 mg, 0.125 mmol) were added in a solution of 6 mL DMF and 2 mL H_2O under stiring, then the solution was transferred in to a 15 mL autoclave. The system was heated at 80^{o}C in oven for 24h and cooled to room temperature at a rate of 1^{o}C/min, where upon the blue bock-shaped crystals of **1** were produced (yield: 48.9 mg, 0.068mmol, 81.6 % based on $Cu(NO_3)_2 \cdot 3H_2O$. The solid product was washed with MeOH, and dried in air.

Crystallographic Data Collection and Refinement

The diffraction data of **1**was collected on an Agilent Technology Super Nova Dual Atlas CCD diffractometer, equipped with monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K. The intensity data were corrected for Lorentz and polarization effects (SAINT), and empirical absorption corrections based on equivalent reflections were applied (SADABS).[1]The structures was solved by direct methods and refined by the full-matrix least-squares method on F^2 with SHELXTL program package.[2]Allnonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were calculated and refined as a riding model. The hydrogen atoms of coordinated water molecules were located from difference maps. The disordered guest molecules in **1** could not be modeled and were treated by the SQUEEZE routine,[3] and the guest molecules were further confirmed by TG and elemental analyses. The crystallographic details are provided in Table S1, and selected bond lengths and angles are given in Table S2. CCDC reference number 1435160, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Drug loading release experiment

Compound **1** was heated under vacuum condition in 140^{o}C for 1.5h to get the activated sample, and then the activated samples were immersed in a hexane solution of ibuprofen (0.012g/mL) and the anethole and guaiacol solution to get the drug loading samples: **1**@ibuprofen, **1**@ anethole and **1**@guaiacol, respectively.

Drug release experiment

The drugs release experiments were performed in the media of water solution, the drug release process were monitored by UV-Vis spectroscopy, while the dosage of the drug-loading sample was unified in 3 mg and the volume of the solution is 3 mL.

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	C46H28Cu3N2O13
Formula weight	1007.32
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, $I4_1/amd$
Unit cell dimensions	a = 19.2590(2)Å $\alpha = 90^o$
	c = 61.2256(12) Å $\gamma = 90^o$
Volume	22709.2(6) Å^3
Z, Calculated density	8, 0.589 Mg/m^3
Absorption coefficient	0.583 mm^{-1}
F(000)	4072
Crystal size	0.50 × 0.26 × 0.24 mm
Theta range for data collection	1.64 to 26.37 deg.
Limiting indices	-20<=h<=19, -19<=k<=24, -66<=l<=76
Reflections collected / unique	31618 / 6161 [R(int) = 0.0393]
Completeness to theta = 26.37	99.9 %
Max. and min. transmission	0.8728 and 0.7593
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6161 / 0 / 153
Goodness-of-fit on F^2	1.131
Final R indices [I>2sigma(I)]	R_1 = 0.0403, wR_2 = 0.1474
R indices (all data)	R_1 = 0.0456, wR_2 = 0.1497
Largest diff. peak and hole	0.712 and -0.559e.Å^3

Table S2 Selected bond lengths [Å] and angles [deg] for **1**.

Cu(1)-O(2)#1	1.9531(16)	O(2)#1-Cu(1)-O(2)#2	87.80(11)
Cu(1)-O(2)#2	1.9531(16)	O(2)#1-Cu(1)-O(3)#3	90.72(8)
Cu(1)-O(3)#3	1.9589(16)	O(2)#2-Cu(1)-O(3)#3	169.10(7)
Cu(1)-O(3)	1.9589(16)	O(2)#1-Cu(1)-O(3)	169.10(7)
Cu(1)-N(1)	2.146(3)	O(2)#2-Cu(1)-O(3)	90.72(8)
Cu(1)-Cu(1)#1	2.5976(7)	O(3)#3-Cu(1)-O(3)	88.70(11)
Cu(2)-O(4)#4	1.9519(17)	O(2)#1-Cu(1)-N(1)	96.14(7)
Cu(2)-O(4)	1.9519(17)	O(2)#2-Cu(1)-N(1)	96.14(7)
Cu(2)-O(4)#5	1.9519(17)	O(3)#3-Cu(1)-N(1)	94.76(7)
Cu(2)-O(4)#6	1.9519(17)	O(3)-Cu(1)-N(1)	94.76(7)
Cu(2)-O(5)	2.115(4)	O(4)#4-Cu(2)-O(4)	89.26(12)
O(2)-Cu(1)#1	1.9531(16)	O(4)#4-Cu(2)-O(4)#5	89.47(12)
O(4)#5-Cu(2)-O(4)#6	89.26(12)	O(4)-Cu(2)-O(4)#5	167.90(10)
O(4)#4-Cu(2)-O(5)	96.05(5)	O(4)#4-Cu(2)-O(4)#6	167.90(10)
O(4)-Cu(2)-O(5)	96.05(5)	O(4)-Cu(2)-O(4)#6	89.47(12)
Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1, #2 x, -y+1, -z+1, #3 -x+1, y, z, #4 -x+2, y, z, #5 -x+2, -y+3/2, z+0, #6 x, -y+3/2, z #7 y+1/4, -x+7/4, -z+5/4, #8 y+1/4, x-1/4,-z+5/4.			

Table S3 C, H, N Elemental analysis for the drug loading samples of **1**.

	1@ibuprofen	**1**@anethole	**1**@guaiacol
Observed C, H, N content	C(65.22%), H(5.76%), N(1.48%)	C(65.53%), H(4.75%), N(1.91%)	C(60.81%), H(4.45%), N(1.28%)
Calculated C, H, N content	C(65.37%), H(5.93%), N(1.66%)	C(65.29%), H(4.71%), N(1.77%)	C(60.43%), H(4.13%), N(1.74%)
Experimental Formula	$[Cu_3(L)_2(pyz)]\cdot 2.7$hexane$\cdot 2.3$ibuprofen	$[Cu_3(L)_2(pyz)]\cdot 4$anethole	$[Cu_3(L)_2(pyz)]\cdot 5$guaiacol
Drug loading	0.45 g/g	0.62 g/g	0.60 g/g

2. Figure S1–S13

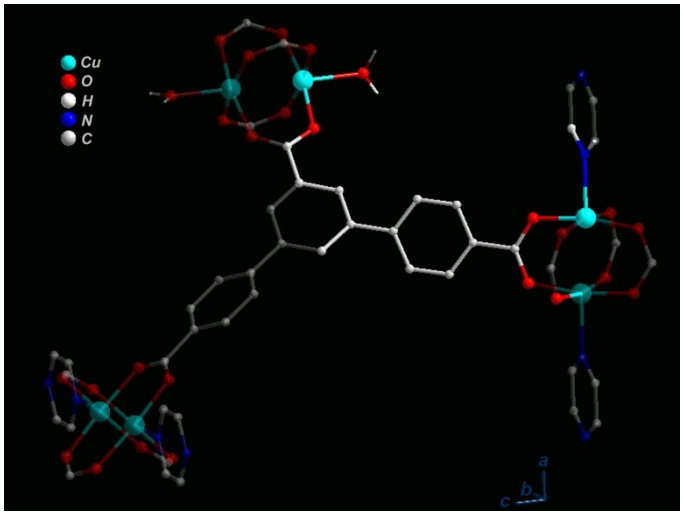

Figure S1 The asymmetry structural unit of **1**.

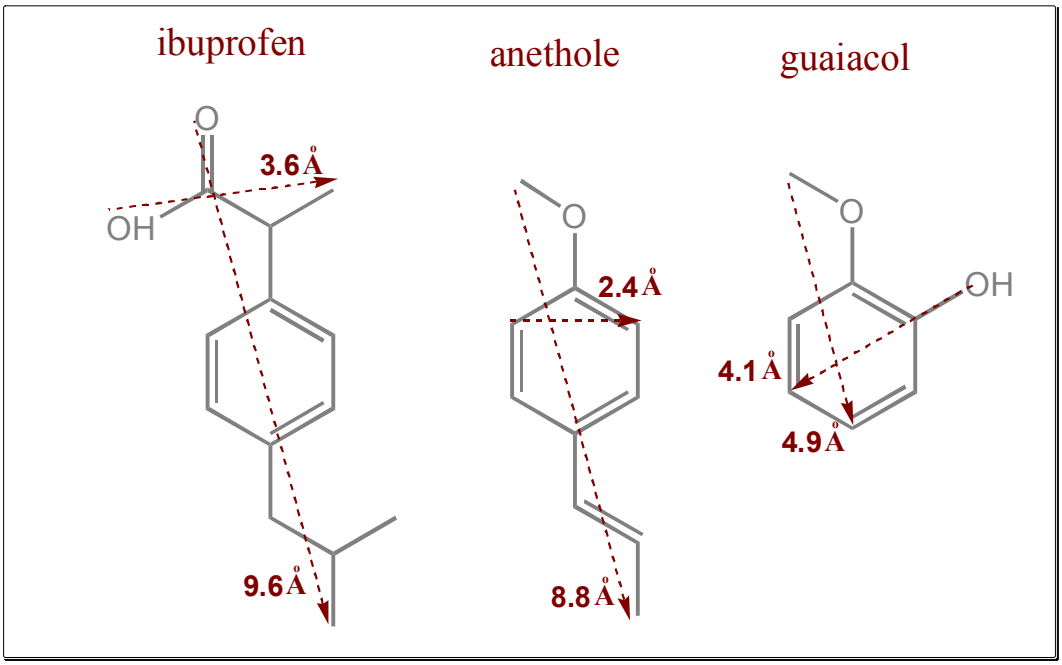

Figure S2 Molecule structure and molecule size of ibuprofen,[4] anethole[5] and guaicaol[6] (molecule size were calculated from the reported cif data by measuring the corresponding atom distance).

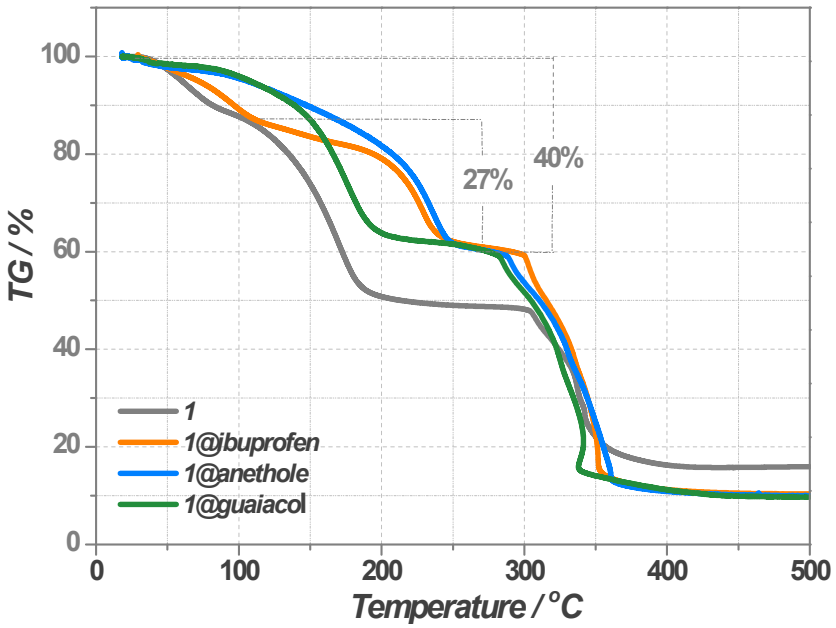

Figure S3 TG curves of sample **1**, drug-loading sample **1**@ibuprofen, **1**@anethole and **1**@guaiacol.

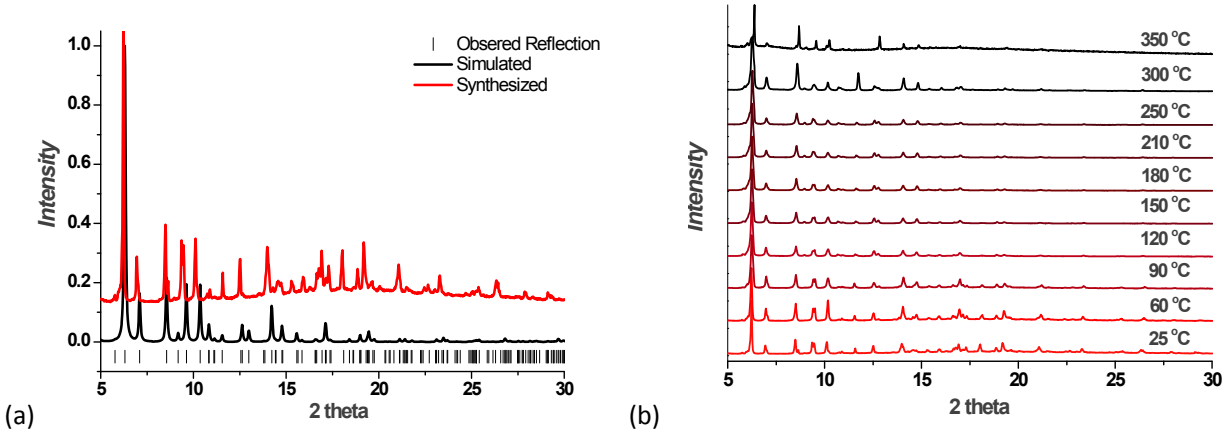

Figure S4 PXRD pattern (a) and Variable-temperature PXRD patterns (b) for **1**.

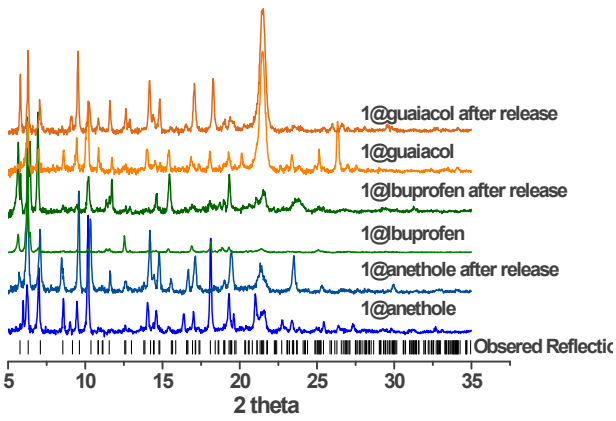

Figure S5 PXRD patterns for drug loading sample of **1**@ibuprofen, **1**@anethole,**1**@guaiacol and the corresponding PXRD pattern for those after the drug molecules were released from the frameworks.

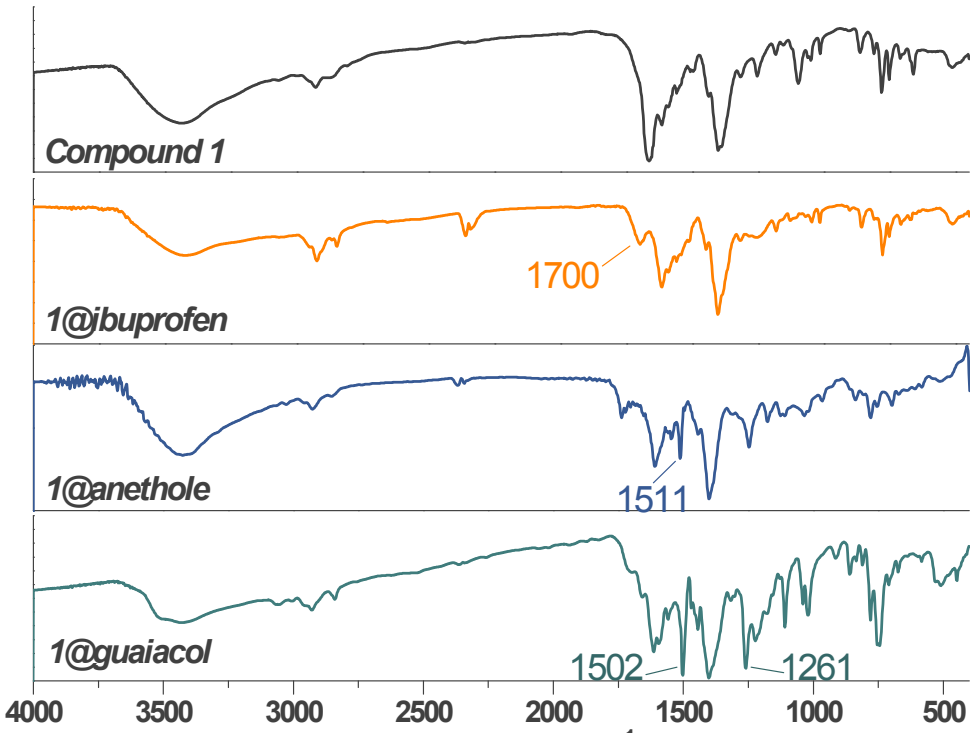

Figure S6 IR spectrum of sample **1**, drug-loading sample of **1**@ibuprofen, **1**@anethole and **1**@guaiacol.

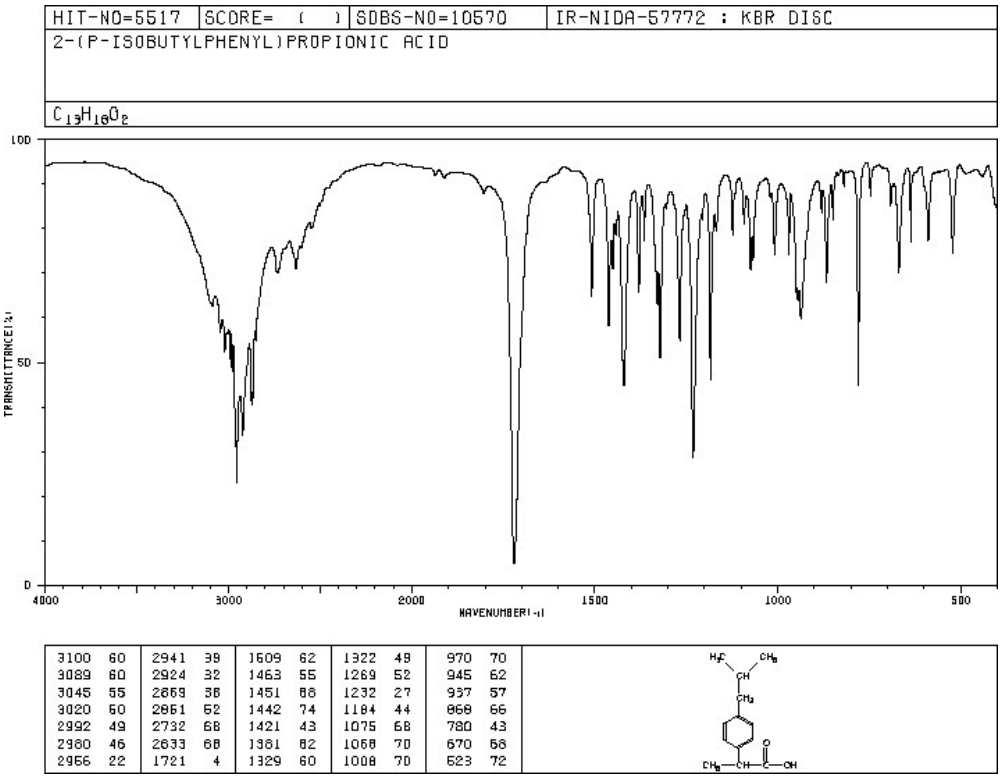

Figure S7 IR spectrum of ibuprofen, indexed from Spectral Database for Organic Compounds, SDBS (organized by National Institute of Advanced Industrial Science and Technology (AIST), Japan).

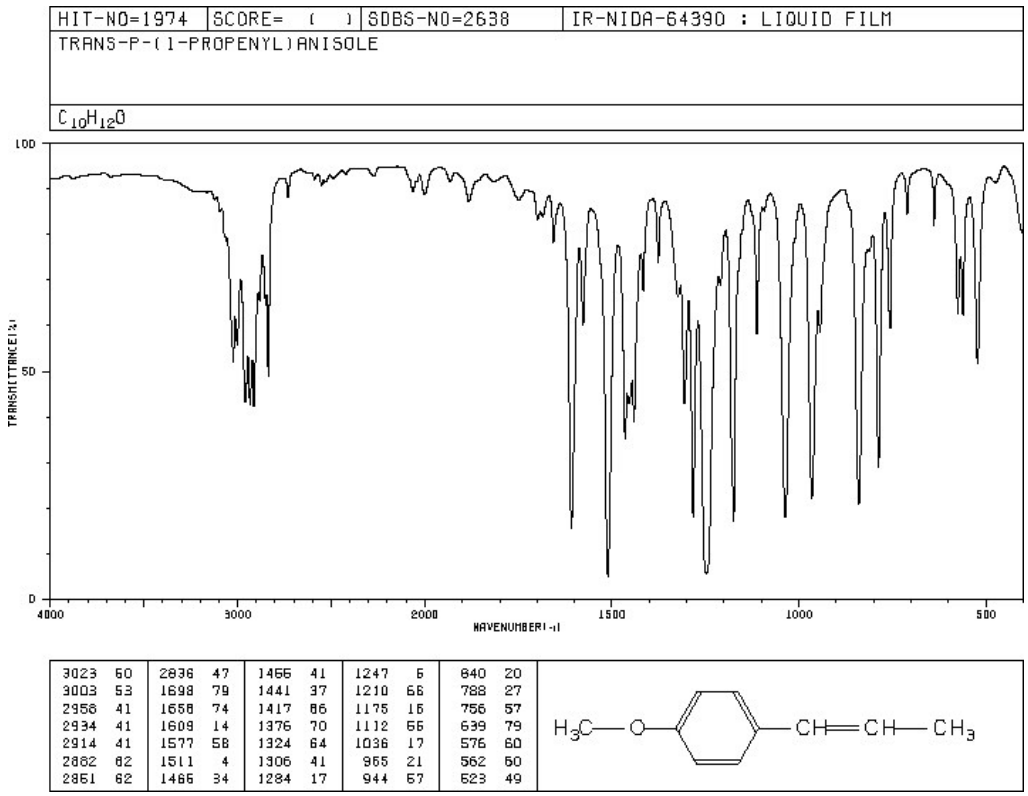

Figure S8 IR spectrum of anethole, indexed from Spectral Database for Organic Compounds, SDBS (organized by National Institute of Advanced Industrial Science and Technology (AIST), Japan).

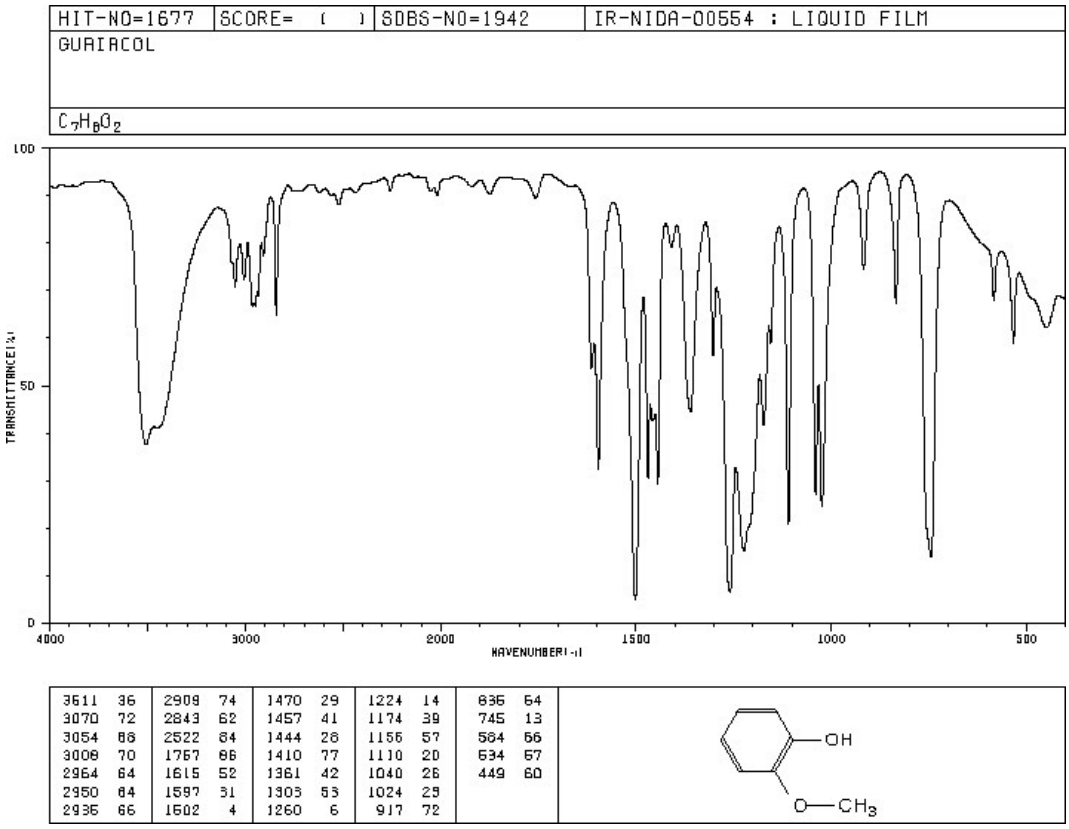

Figure S9 IR spectrum of guaiacol, indexed from Spectral Database for Organic Compounds, SDBS (organized by National Institute of Advanced Industrial Science and Technology (AIST), Japan).

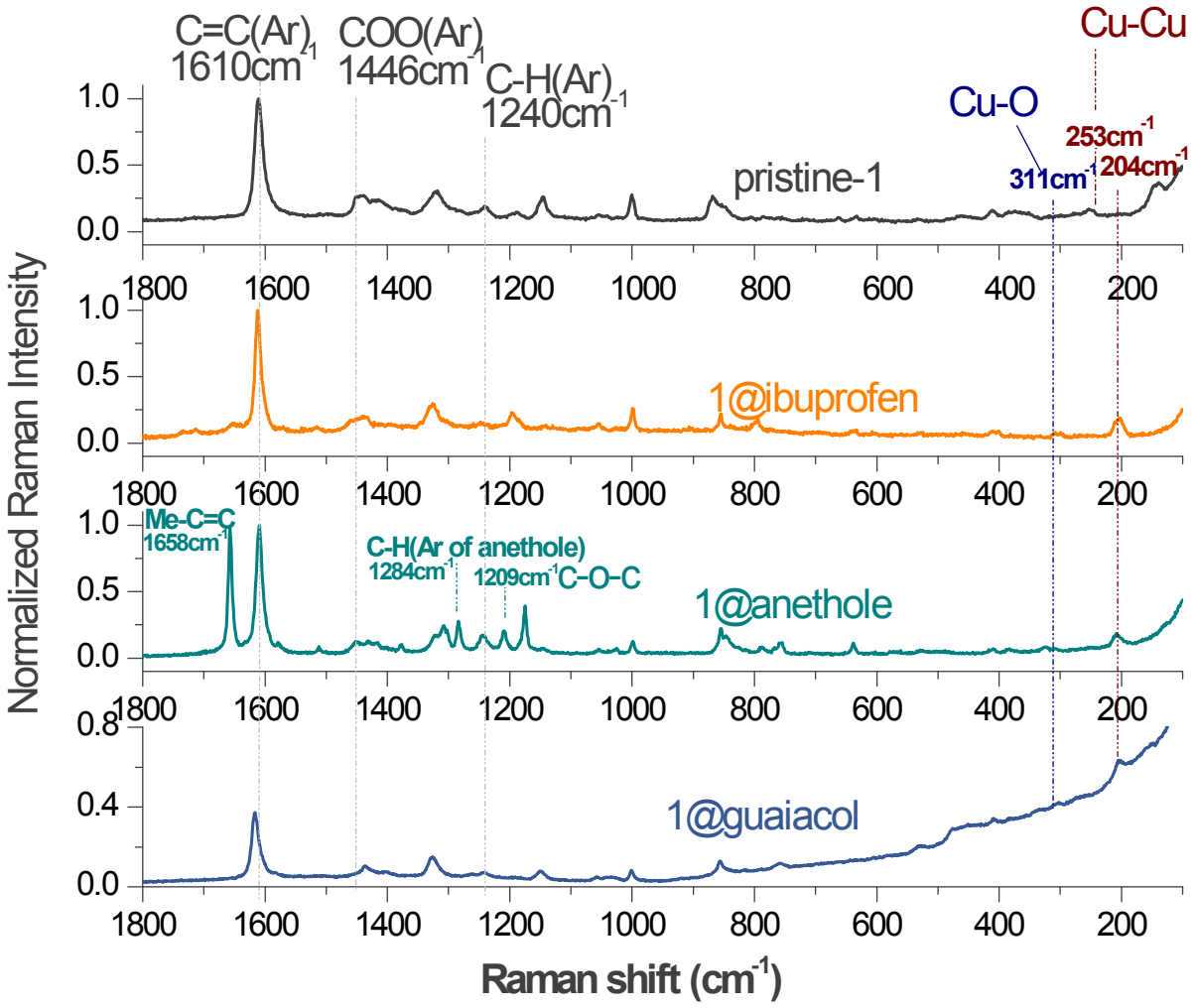

Figure S10 Raman spectrum of sample **1**, drug-loading sample of **1**@ibuprofen,[7,8]**1**@anethole[7,8,9] and **1**@guaiacol.[7,8]

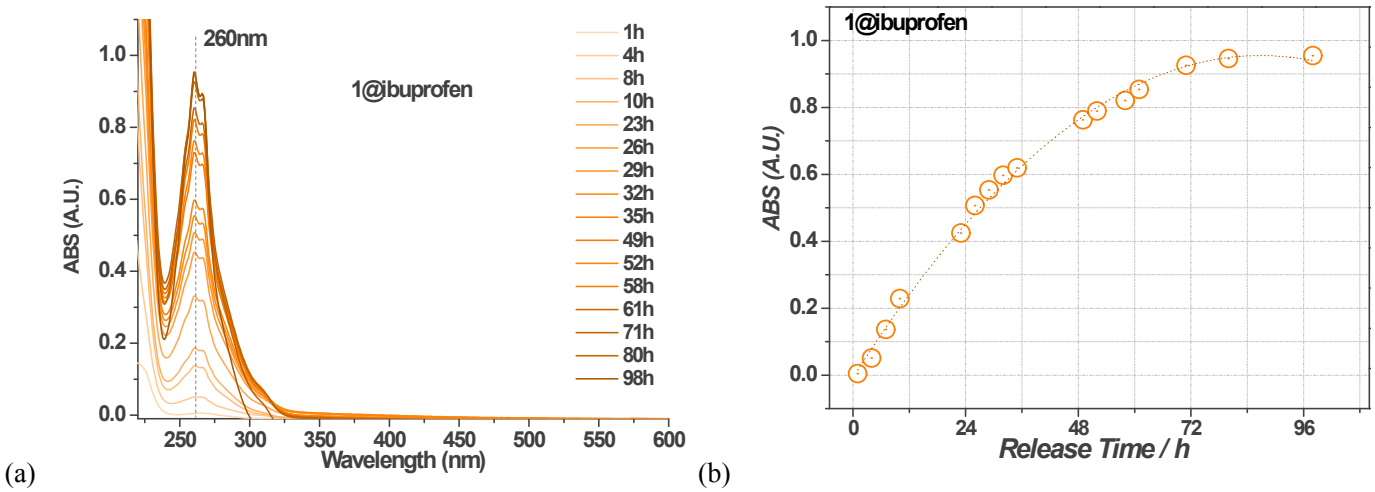

Figure S11 (a) UV–Vis spectrum of sample **1**@ibuprofen release in H_2O in a time scale of 0-98 h; (b) the dynamic curve of absorbance in the characteristic wavelength of 260 nm changed with the time.

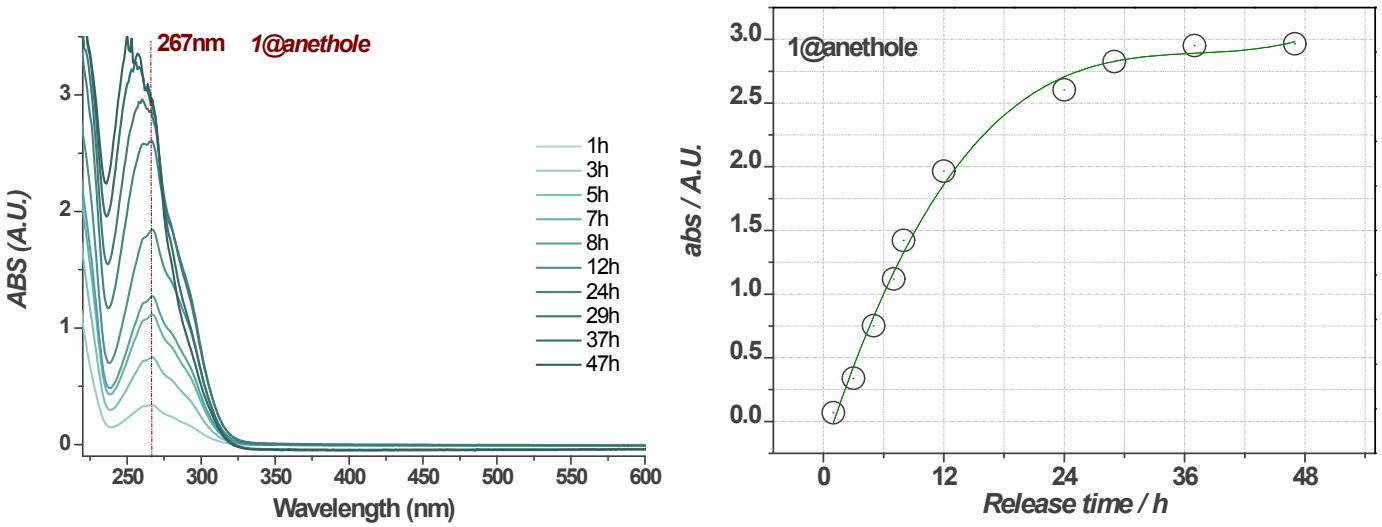

Figure S12 (a) UV–Vis spectrum of sample **1**@anethole release in 3 mL water in a time scale of 0-47 h; (b) the dynamic curve of absorbance in wavelength of 267 nm changed with the time.

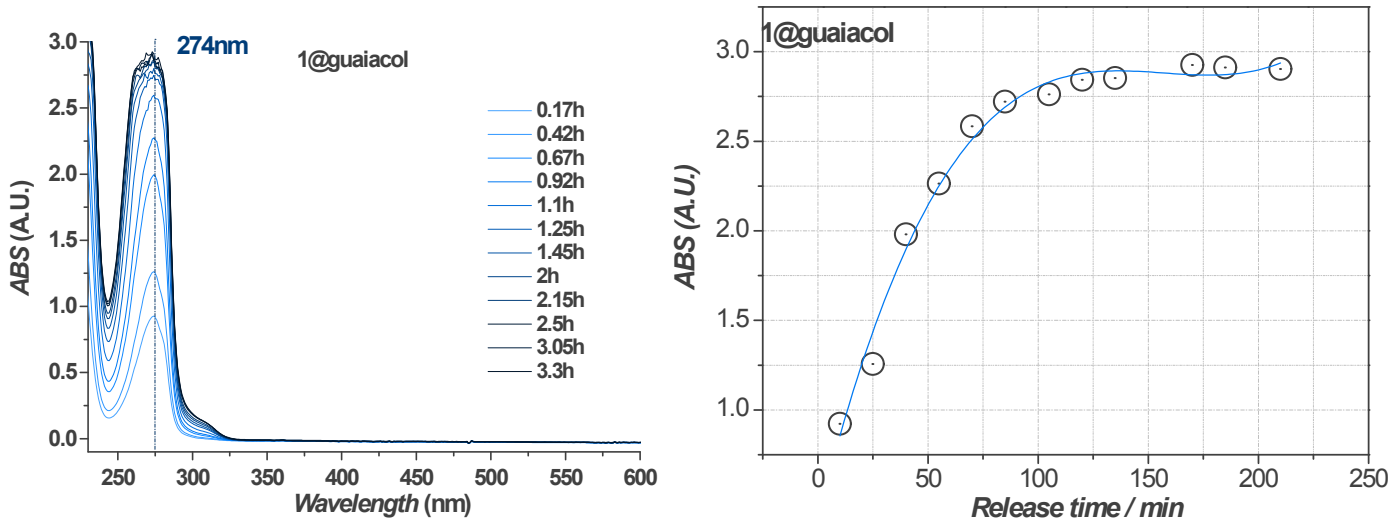

Figure S13 (a) UV–Vis spectrum of sample **1**@guaiacol release in 3 mL water in a time scale of 0-3.3 h; (b) the dynamic curve of absorbance in wavelength of 274 nm changed with the time.

Reference

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