

Supporting information

A cucurbit[6]uril-based supramolecular assembly as a highly sensitive and quickly responsive luminescent sensor for the detection of fluoroquinolones antibiotics in simulated wastewater

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Experimental

Materials and measurements

CB[6] was synthesized by literature method [1] and other chemicals employed were commercially purchased, and used directly without further purification. The urine used in this work was prepared according to previously reported methods [2, 3]. Powder X-ray diffraction (PXRD) measurements were obtained on a Rigaku/Dmax 2200 pc X-ray diffractometer using Cu-K α radiation in the angular range of 2θ from 5° to 50° . Thermogravimetric analysis (TGA) was taken on a Netzsch STA449F3 analyzer at a heating rate of 5°C min^{-1} from 25-800 $^\circ\text{C}$ under the nitrogen atmosphere. Luminescent spectra were recorded on an Edinburgh FLS55 spectrophotometer. The slit widths of both excitation and emission monochromators were set to 5 nm. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer.

*Synthesis of $[\text{Na}_4\text{CB}[6](\text{H}_2\text{O})_{10}\text{DMF}]\cdot 2\text{BPDS}\cdot 2\text{H}_2\text{O}$ (**1**)*

A mixture of NaCl (0.5 mmol), CB[6] (0.05 mmol), H₂BPDS (0.25 mmol), and 1, 2, 4-Triazole (0.25 mmol) was dissolved in ultrapure water (H₂O) and N, N-dimethylformamide (DMF) mixed solvent (4 mL, v/v:3/1), and then the solution was sealed in a 10 mL Teflon-lined stainless steel autoclave and maintained at 120 $^\circ\text{C}$ for 2 days, followed by refrigeration to room temperature at a rate of 5°C h^{-1} . Colourless crystals of compound **1** were collected by filtration, washed with pure water.

X-ray crystallography

Single-crystal X-ray data of **1** was collected on a Bruker APX-II CCD area-detector

diffractometer with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 273.15 K during data collection. Data reduction was performed using SAINT program and corrected for Lorentz and polarization effects. Adsorption correction was performed using the SADABS program [4]. The structure was solved by direct methods using the program SHELXS-2015 and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique with SHELXL-2015 [5]. The highly disordered free solvent molecules in the unit cell have been subtracted from the diffraction data with the SQUEEZE subroutine of the PLATON program [6]. The positions of hydrogen were placed geometrically and refined with isotropic thermal parameters riding on those parent atoms. The details of the crystal parameters, data collection, and refinements for **1** were given in Table S1. These data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1976791.

Fluorescence sensing methodology

The standard suspensions were prepared by adding the powder sample of **1** (2 mg) into ultrapure water (9 ml), and the resulting mixture was mixed by ultrasonication for 10 min. The test sample for the selective experiment was carried out by adding different antibiotics (1 mM, 0.5 ml) to **1** suspensions and making the final solution volume to 10 mL. Luminescence titration experiments were performed by adding analytes to **1** suspension. The excitation wavelength (λ_{ex}) was 285 nm, while the slit widths of both excitation and emission monochromators were set to 5 nm to maintain consistency.

Recycle experiment

The recycling experiments were carried out as following procedures: 30 mg powder of **1** was soaked in 10 μ M different analytes solutions for one day, then the analytes loaded **1** phase was centrifuged followed by washing with distilled water to recover a crystalline phase which was used for the next cycle.

Anti-interference experiment

The standard suspensions were prepared similarly as mentioned above. The concentration and volume for both GAT and the interfering antibiotics were 1 mM and 0.5 mL, they were added to the standard suspensions and making the final solution volume to 10 mL. The effect of major chemicals existing in wastewater (such as Co^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+} , Cr^{3+}) and urine (such as urea, glucose, creatinine, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}) were investigated by dispersing **1** (2 mg) into corresponding aqueous solutions (1 mM, 10 ml), then added GAT (1 mM, 0.5 ml) to the suspensions.

References

- [1] J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, J. Am. Chem. Soc. 122 (2000) 540-541.
- [2] S.-J. Qin, B. Yan, Sens. Actuators. B 259 (2018) 125-132.
- [3] N. Brunzel, Chemical examination of urine and automation in the urinalysis Laboratory. Fundamentals of urine and Body fluid analysis, Philadelphia: WB Saunders Company, p65-70. Prosiding Konferensi Nasional Ke-7, 1994
- [4] G.M. Sheldrick, SADABS, Program for Empirical Adsorption Correction of Area

Detector Data, University of Göttingen, Göttingen, Germany, 2003.

[5] (a) G.M. Sheldrick, SHELXS-2016, Program for the Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 2016; (b) G.M. Sheldrick, SHELXL-2016, Program for the Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 2016.

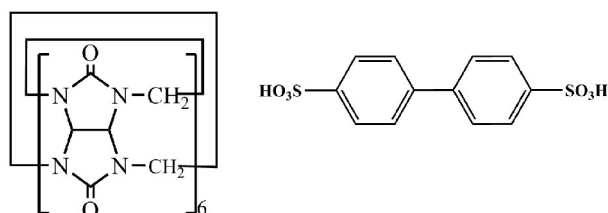
[6] (a) A. L. Spek, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 1990, 46, 194; (b) A. Platon, J. Appl. Crystallogr. 36 (2003) 7.

Crystallographic data for **1** has been deposited with the Cambridge Crystallographic Data Centre with No. CCDC 1976791. Copies of the data can be obtained free of charge via the Internet at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or by post at CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223336033, E-mail: deposit@ccdc.cam.ac.uk).

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

Compound	[Na ₄ CB[6](H ₂ O) ₁₀ DMF]·2BPDS·2H ₂ O
Empirical formula	C ₆₃ H ₈₃ N ₂₅ Na ₄ O ₃₇ S ₄
Formula weight	2002.74
Crystal system	Monoclinic
Space group	P2 ₁ /n
a (Å)	11.2749(9)
b (Å)	24.769(2)

c (Å)	14.9058(12)
α (°)	90
β (°)	92.691(2)
γ (°)	90
V (Å ³)	4158.2(6)
Z	2
D_c /(g cm ⁻³)	1.600
μ /(mm ⁻¹)	0.245
$F(000)$	2080.0
θ range (°)	5.472-50.02
R_{int}	0.0531
Parameters	681
T (K)	273.15
goodness of fit	1.076
Limiting indices	$-13 \leq h \leq 13$ $-29 \leq k \leq 29$ $-17 \leq l \leq 17$
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0927$, $wR_2 = 0.2203$
R indices (all data)	$R_1 = 0.1138$, $wR_2 = 0.2325$



Scheme S1 The chemical structure of CB[6] and H₂BPDS.

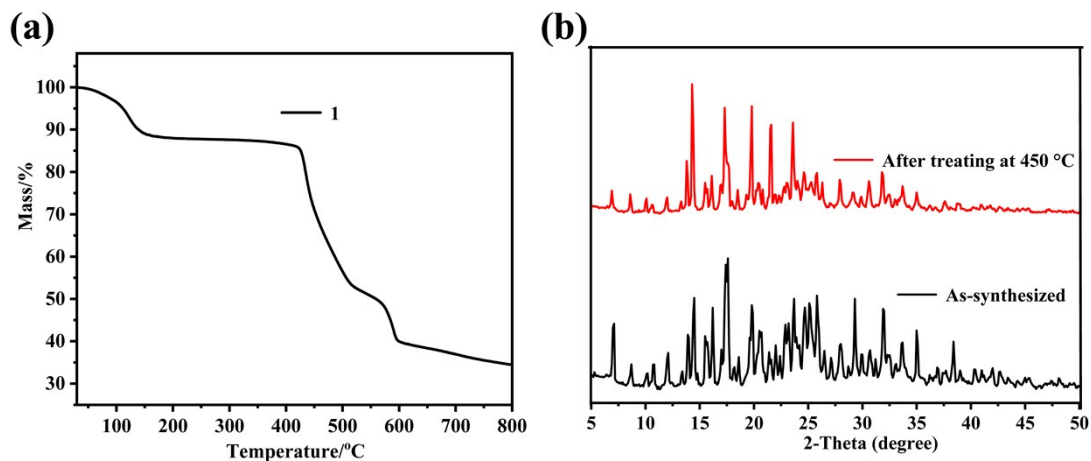


Fig.S1 (a) TGA curves of **1** under atmosphere of N_2 ($5\text{ }^\circ\text{Cmin}^{-1}$); (b) PXRD patterns of **1** as-synthesized and after treating at $450\text{ }^\circ\text{C}$.

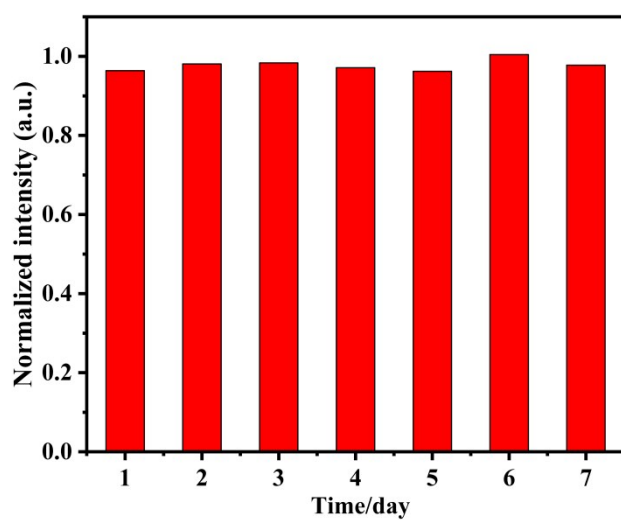


Fig. S2 Luminescence spectra of **1** dispersed in water with different times.

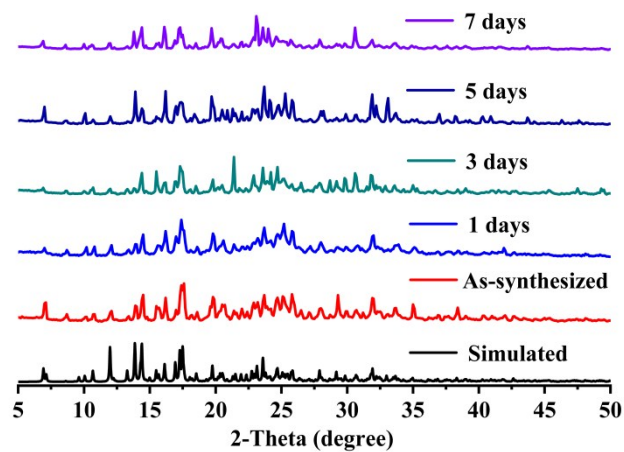


Fig. S3 PXRD patterns of **1** after soaked in water with different times.

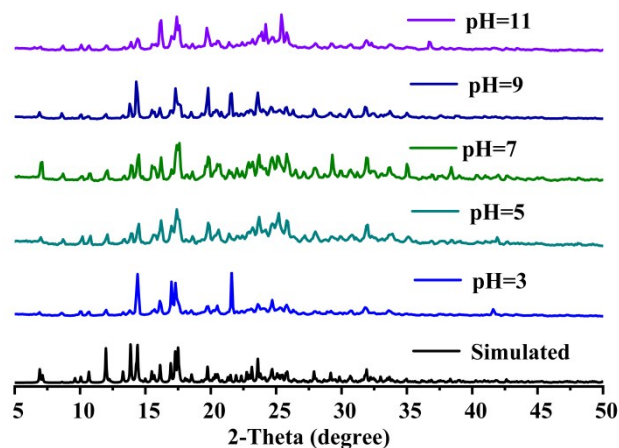


Fig. S4 PXRD patterns of **1** in aqueous solution with different pH value.

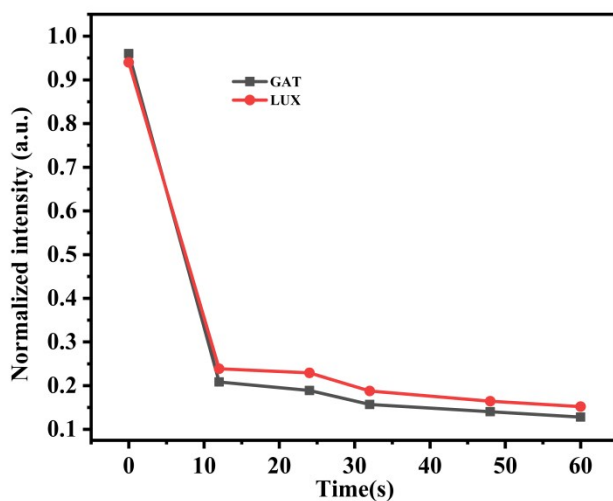


Fig. S5 Luminescence intensity versus time curve of LUX and GAT (50 μ M) in **1** (2mg) suspensions.

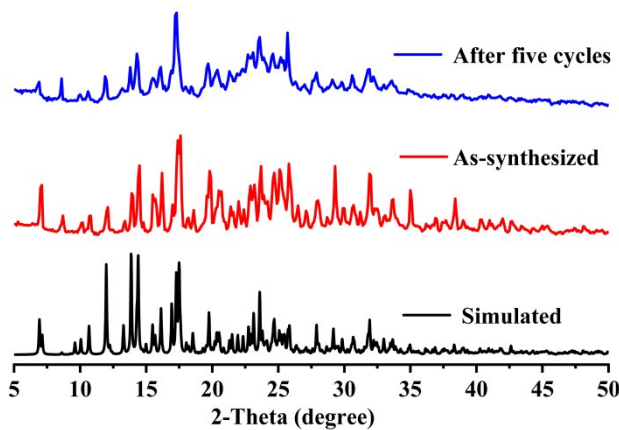


Fig. S6 PXRD patterns of **1** simulated, as-synthesized and after five cycles.

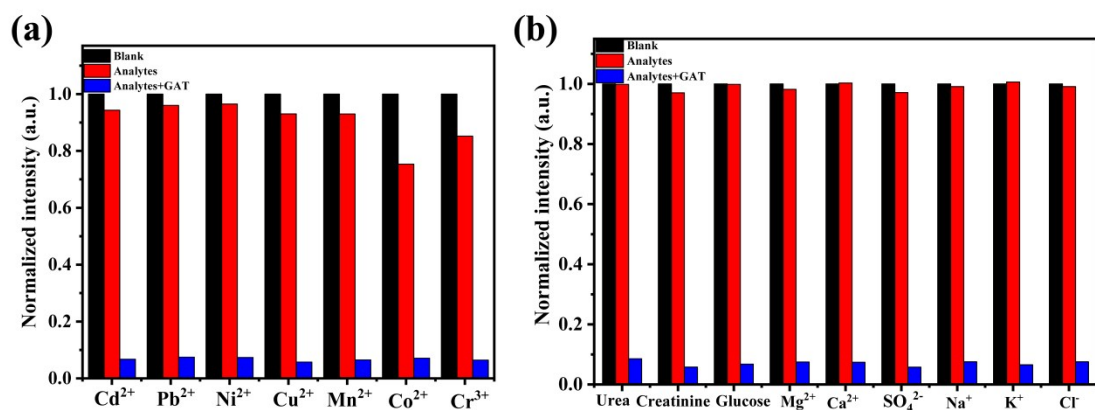


Fig. S7 Fluorescence responses of **1** in simulated wastewater (a) and urine (b) samples.

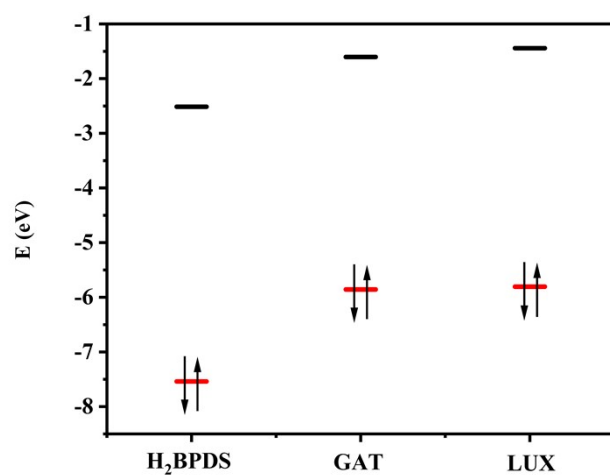


Fig. S8 Theoretical HOMO and LUMO energies for H₂BPDS, LUX and GAT.

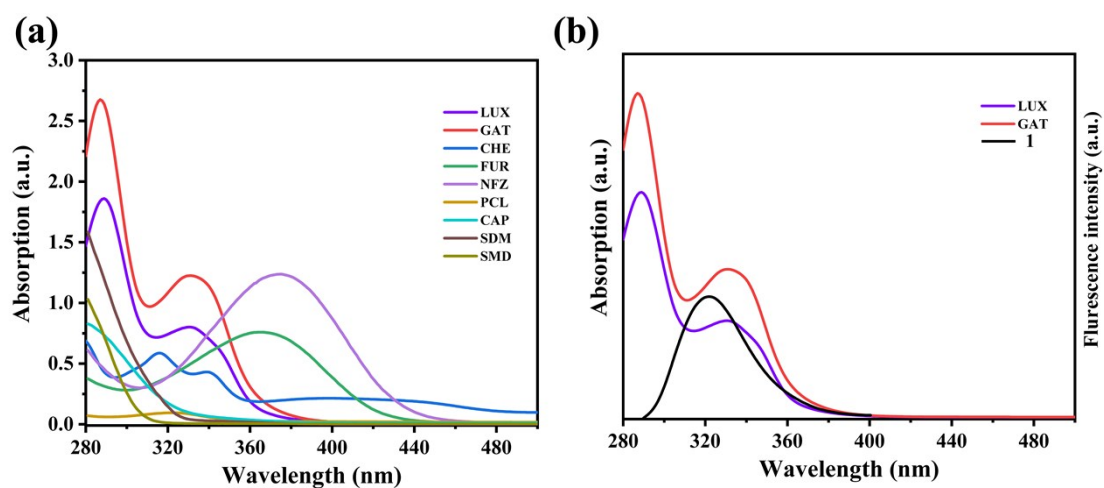


Fig. S9 (a) UV-visible spectra of antibiotics in water; (b) UV-vis absorption spectra of LUX and GAT and emission spectra of **1** in water.

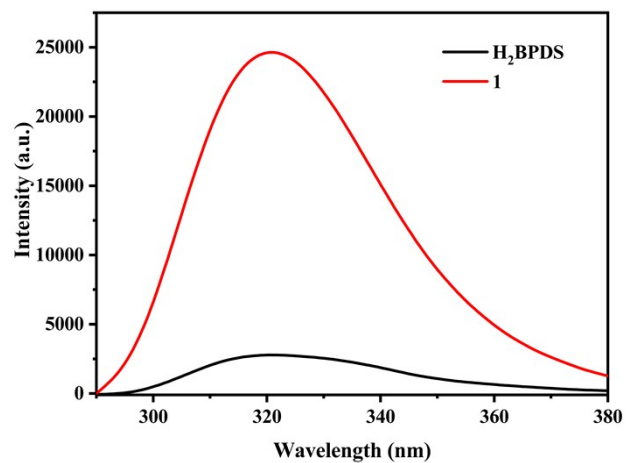


Fig. S10 The luminescent spectrum of **1** and H₂BPDS in solid states.

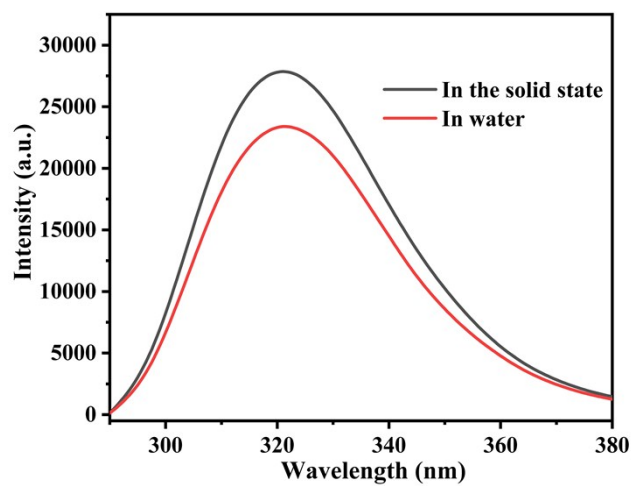


Fig. S11 Solid and suspension luminescence of **1**