A Water Stable and Highly Fluorescent Zn(II) Based Metal−Organic Frameworks for Fast Detection of Hg^{2+}, Cr^{VI} and Antibiotics

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CONTENTS

Materials and methods

With the exception of BBDF, all solvents and materials were purchased without any purification. Powder X-ray diffraction (XRD) were performed on Bruker D2 PHASER diffractometer with Cu-$K\alpha$ radiation (λ= 1.54186 Å). Thermogravimetric analysis was carried out with a NETZSCH STA 449F5 (TG/DTA) thermal analyzer under nitrogen flow. IR spectra of the two compounds were performed on a Bruker AXS TENSOR-27 FT-IR spectrometer (FTIR) with pressed KBr pellets in the range of 4000–400 cm^{-1}. Fluorescence measurements were carried out on an F4700 (Hitachi) fluorescence spectrophotometer at room temperature. UV-vis absorption analysis was performed on a U-3010 spectrophotometer at room temperature.

Crystallographic studies

Single-crystal X-ray diffraction data of **1** were collected on a Bruker APEX-II CCD with ω-scan pattern and Ga-Kα radiation (λ = 1.34139 Å) at 200 K. The structures were solved with direct methods (SHELX), and refined by fullmatrix least squares on F^2 using OLEX3, which utilizes the SHELXL-2018 module. The hydrogen atoms were placed geometrically. All non-hydrogen atoms were refined anisotropically. The H atoms of ATP^{2-} and BBDF were generated from the computed positions and subjected to isotropic refinement. The guest DMF molecules and water molecules are too disordered to be modeled properly. So the diffuse electron densities resulting from these solvent molecules are removed by using the SQUEEZE routine of PLATON program to produce solvent-free diffraction intensities. The guest molecules were quantified through the elemental analyses and thermogravimetric analyses. The relevant crystallographic data are summarized in Table 1. The chosen bond lengths as well as angles are presented in Table S2.

Fluorescence Measurements

Luminescent spectra were recorded with a F4700 (Hitachi) fluorescence spectrophotometer at room temperature. The cation incorporated **1** emulsions were prepared by introducing 3 mg of **1** powder into 3.00 mL of aqueous solution containing K^+, Na^+, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}, Ag^+, Co^{2+}, Ni^{2+}, Mg^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+} and Cr^{3+} at a concentration of 0.1 mM. For sensing properties with respect to Hg^{2+}, 3 mg of 1 powder was dispersed in 3.00 mL of Hg^{2+} aqueous solution with different concentrations. The anions incorporated **1** emulsions were prepared by introducing 3 mg of 1 powder into 3.00 mL of sodium salts aqueous solution of NO_2^-, Br^-, I^-, Cl^-, $H_2PO_4^-$, SO_4^{2-}, NO_3^-, WO_4^{2-}, Ac^-, SCN^-, HPO_4^{2-}, HCO_3^-, CO_3^{2-}, $Cr_2O_7^{2-}$ and CrO_4^{2-} at a concentration of 0.5 mM. For sensing properties with respect to $Cr_2O_7^{2-}$, 3 mg of 1 powder was added into 3.00 mL of $Cr_2O_7^2$ aqueous solution with different concentrations.

The antibiotics incorporated **1** emulsions were prepared by introducing 3 mg of **1** powder into 3.00 mL of sodium salts aqueous solution of NFZ, NFT, ODZ, RDZ, MDZ, DTZ, SMZ, SDZ, STZ, CAP, CPF and LOF at a concentration of 0.2 mM. For sensing properties with respect to

$Cr_2O_7^{2-}$, 3 mg of **1** powder was added into 3.00 mL of NFZ or NFT aqueous solution with different concentrations. The finely ground powder of complex **1** is dispersed well in the solution, which enables substrates to be closely adhered to the surface of the MOF particles and facilitates possible host–guest interactions. To obtain the luminescent spectra, the emulsions were treated by ultrasonic treatment for 30 min to form stable emulsions before fluorescence study. Each PL emission spectra were measured at least three times and the emission intensities were found basically unvaried.

Synthesis of BBDF

A flame-dried Schlenk flask was charged with A mixture of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (3.52 g, 10 mmol), benzimidazole (5.90 g, 50 mmol),, K_2CO_3 (10.00 g, 72 mmol), CuI (0.44 g, 2.3 mmol) and DMF(100 mL) at room temperature under nitrogen. After being heated at 120 ºC for 72 h, the mixture was evaporated under vacuum. Thereafter, 100 mL of distilled water was added to facilitate the workup. The mixture was extracted three times with CH_2Cl_2 (100 mL), then the organic phase was further washed with distilled water and dried with anhydrous $MgSO_4$. After the filtration and evaporation, the resulting residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH (20: 1) to give BBDF as a pale-yellow solid. Isolated yield: 2.3 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (s, 6H), 7.38 (d *J* = 5.1 Hz, 5H), 7.55-7.62 (m, 6H), 7.97 (d *J* = 8.1 Hz,4H), 8.28 (s, 2H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 27.1, 47.7, 110.6, 118.7, 120.8, 121.7, 122.9, 123.4, 135.9, 137.9, 155.8 ppm. Yellow block crystals of BBDF were obtained by recrystallization in the mixed solvent of DMF and H_2O. The detailed crystal data and structure refinement parameters are shown in Table 1.

Table S1 Selected bond lengths (Å) and angles (°) for **1**

Zn1-O1	2.1434(15)	Zn1-O2	2.2647(18)
Zn1-O3#1	2.176(2)	Zn1-O4#1	2.254(2)
Zn1-N2	2.0430(16)	Zn1-N5#2	2.0721(16)
O1-Zn1-O2	59.57(6)	O1-Zn1-O3#1	101.54(7)
O1-Zn1-O4#1	150.36(8)	O3-Zn1-O2#1	89.26(7)
O3#1-Zn1-O4#1	58.58(8)	N2-Zn1-O1	106.48(6)
O4-Zn1-O2	96.00(7)	N2-Zn1-O2	94.34(6)
N5-Zn1-O1#2	93.29(6)	N2-Zn1-O3#1	149.37(8)
N5-Zn1-O2#2	152.38(6)	N2-Zn1-O4#1	90.80(7)
N5#2-Zn1-O3#1	91.66(7)	N2-Zn1-N5#2	98.74(7)
N5#2-Zn1-O4#1	107.97(7)		
Symmetry codes: #1: x, 1-y, -1/2+z #2: -1+x, y, z			

Table S2 SHAPE analysis of the Zn^{II} ions in **1**.

ions	label	shape	symmetry	distortion(τ)
	HP-6	Hexagon	D_{6h}	32.122
	PPY-6	Pentagonal pyramid	C_{5v}	19.092
Zn1	OC-6	Octahedron	O_h	**5.715**
	TPR-6	Trigonal prism	D_{3h}	10.611
	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	23.320

Table S3 Comparison of **1** with recent MOF-based luminescent sensors for Hg^{2+}.

MOF-based chemosensor	Analyst	$K_{sv} \times 10^4$ /M^{-1}	LOD	Medium	Ref.
$[Zn(\mu_2\text{-}1H\text{-ade})(\mu_2\text{-}SO_4)]_n$	Hg^{2+}	0.77	0.07 μM	H_2O	1
$[Zn_2(bbmb)_2(tdc)_2] \cdot 2H_2O$	Hg^{2+}	48.1	0.19 μM	H_2O	2
$Cd_3(C_{10}H_4O_7N_1)_2(H_2O)_8]$ $0.733(O_2) \cdot 2(H_{1.47} O_{0.27})$	Hg^{2+}	11.4	5.4 ppb	H_2O	3
$\{[Cd_{1.5}(C_{18}H_{10}O_{10})] \cdot (H_3O)(H_2O)_3\}n$	Hg^{2+}	0.43	NR	H_2O	4
$Eu^{3+}@UIO\text{-}66(DPA)$	Hg^{2+}	137	8.26 nM	H_2O	5
$[Zn(2\text{-}NH_2bdc)(bibp)]n$	Hg^{2+}	655	4.2×10^{-8} M	H_2O	6
$\{[Cd(BIBT)(TDC)] \cdot 2H_2O\}n$	Hg^{2+}	5.05	0.097 μM	H_2O	7
$[Zr_6O_4(OH)_4(C_{12}H_4S_2)_{4.9}] \cdot 4H_2O \cdot 4DMF$	Hg^{2+}	35.4	5 nM	H_2O	8
$[Zn_3(ssa)_2(1,4\text{-}bib)_3 \cdot 4H_2O]n$	Hg^{2+}	19.8	0.23 μM	H_2O	9
$[Cd(L)(NTA)]n$	Hg^{2+}	0.357	3.05 μM	H_2O	10
$[Ni(L)(NPTA) H_2O]n$		0.743	2.29 μM		
$\{[Cd(BIPA)(tfbdc)(H_2O)] \cdot DMF\}n$	Hg^{2+}	1.27	0.12 μM	H_2O	11
$[Co(NPDC)(bpee)] \cdot DMF \cdot 2H_2O$	Hg^{2+}	0.426	4.1 μM	H_2O	12
$\{[Zn(BBDF)(ATP)] \cdot 2DMF \cdot 3H_2O\}_n$	**Hg^{2+}**	**3.89**	**0.12 μM**	H_2O	**this work**

Table S4 Comparison of **1** with recent MOF-based luminescent sensors for $Cr_2O_7^{2-}$ and CrO_4^{2-}
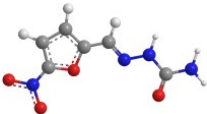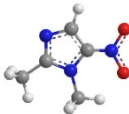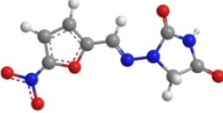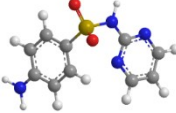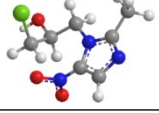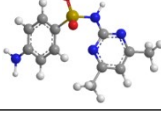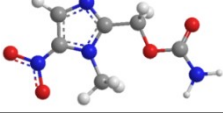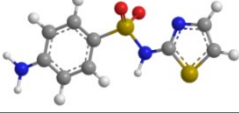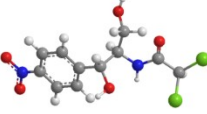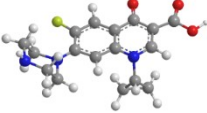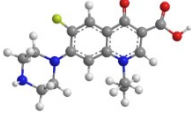
MOF-based chemosensor	Analyst	$K_{SV} \times 10^4$ /M^{-1}	LOD	Medium	Ref.
Zn-(PBBA)(H$_2$O)]·3DMF·2H$_2$O	$Cr_2O_7^{2-}$	1.2	4.2 μM	H$_2$O	13
{[Zn(L)$_{0.5}$(bpea)]·0.5H$_2$O·0.5DMF	$Cr_2O_7^{2-}$	1.65	1.42 μM	H$_2$O	14
	CrO_4^{2-}	1.34	2.65 μM		
{[Zn-(L)$_{0.5}$(ibpt)]·H$_2$O·DMF}$_n$	$Cr_2O_7^{2-}$	1.02	2.21 μM		
	CrO_4^{2-}	1.26	3.78μM		
[Zn(L1)hfdba]n	$Cr_2O_7^{2}$	0.5029	0.33 μM	H$_2$O	15
	CrO_4^{2-}	0.22387	0.745 μM		
{[Zn(L$_2$)(hfdba)$_2$]·2H$_2$O}n.	$Cr_2O_7^{2}$	1.3268	83.5 μM		
	CrO_4^{2-}	0.9079	114.2 μM		
Gd$_{10}$L$_6$(OH)$_4$(H$_2$O)$_3$]·4C$_2$H$_8$N	$Cr_2O_7^{2-}$	NR	2.68 μM	H$_2$O	16
{[Cd(μ_5-L) I}n	$Cr_2O_7^{2-}$	1.85	NR	H$_2$O	17
[Zn(OBA)$_2$(L$_1$)·2DMA]$_n$	$Cr_2O_7^{2-}$	1.897	2.37μM	H$_2$O	18
	CrO_4^{2-}	1.1605	3.87 μM		
[Zn(ttb)(bdc)$_{0.5}$]$_n$	$Cr_2O_7^{2-}$	6.67	0.10 μM	H$_2$O	19
Cd$_3$L(BTB)$_2$·2DMF	$Cr_2O_7^{2-}$	2.06	1.2 μM	H$_2$O	20
(Cd$_3$O$_2$)LBTC		2.44	1.4 μM		
[Zn(L)·2MeOH·H$_2$O]	$Cr_2O_7^{2-}$	0.118	2.95 μM	H$_2$O	21
[Cd$_{1.5}$(L)$_2$(bpy)(NO$_3$)]·2DMF·2H$_2$O	$Cr_2O_7^{2-}$	5.42	320 ppb	H$_2$O	22
	CrO_4^{2-}	1.73	320 ppb		
Zn$_2$(tpeb)(bpdc)$_2$·0.5DMA·4H$_2$O	$Cr_2O_7^{2-}$	1.122	1.04 μM	H$_2$O	23
	CrO_4^{2-}	1.085	1.07 μM		
{[Zn$_3$(mtrb)$_3$(btc)$_2$]·3H$_2$O}n	$Cr_2O_7^{2-}$	0.277	4.52 M	H$_2$O	24
{[Zn(BBDF)(ATP)]·2DMF·3H$_2$O}$_n$	**$Cr_2O_7^{2-}$**	**2.64**	**0.17 μM**	H$_2$O	**this work**

Table S5 Comparison of **1** with recent MOF-based luminescent sensors for NFZ and NFT

MOF-based chemosensor	Analyst	$K_{SV}\times10^4$ /M^{-1}	LOD	Medium	Ref.
{[Eu$_2$Na(Hpdbb)(pdbb)$_2$ (CH$_3$COO)$_2$]·2.5DMA}$_n$	NFZ	4.85	0.64 μM	DMF	25
	NFT	4.39	0.68 μM		
[Cd$_2$(L$_2$)(bpda)$_2$]·3DMF·H$_2$O	NFZ	3.1	1.27 μM	DMF	26
	NFT	2.2	1.95 μM		
{[Eu(H$_2$O)(BTCTB)]·2H$_2$O}n	NFZ	1.27	0.67 μM	H$_2$O	27
	NFT	2.1	0.6 μM		
[Eu(cppa)(OH)]·xS	NFT	2.33	0.43 μM	H$_2$O	28
Zr$_6$O$_4$(OH)$_8$(H$_2$O)$_4$(CTTA)$_{8/3}$	NFZ	11	NR	H$_2$O	29
	NFT	3.8	NR		
Zr$_6$O$_4$(OH)$_8$(H$_2$O)$_4$(TTNA)$_{8/3}$	NFZ	7.5	NR		
	NFT	6.0	NR		
[Zn(C$_{18}$N$_2$O$_4$H$_{10}$)H$_2$O]·DMF	NFT	6.0	0.14 μM	Ethanol	30
	NFZ	4.73	0.19 μM		
Cd$_3$·L·(BTB)$_2$·2DMF	NFT	6.81	0.44 μM	DMF	31
Cd$_3$O$_2$)·L·BTC		3.80	0.78 μM		
{[Zn$_2$(TRZ)$_2$(DBTDC-O$_2$)]·DMAc}$_n$	NFZ	4.5	0.404 μM	H$_2$O	32
	NFT	18	0.353 μM		
{[Cd$_2$(Py$_2$TTz)$_2$(BDC)$_2$]·2(DMF)}$_n$	NFZ	4.4	0.85 μM	H$_2$O	33
[Cd$_3$(CBCD)$_2$(DMA)$_4$(H$_2$O)$_2$]·10DMA	NFT	9.72	85 ppb	DMA	34
	NFT	6.39	128 ppb		
RhB@ZIF-8	NFZ	7.3	0.26 μM	H$_2$O	35
	NFT	1.8	0.47μM		
[Zn$_3$(bpg)$_{1.5}$(azdc)$_3$]·(DMF)$_{5.9}$·(H$_2$O)$_{1.05}$	NFZ	8.75	0.66 μM	DMF	36
	NFT	5.92	NR		
{[(CH$_3$)$_2$NH$_2$]$_2$[Pb(TCBPE)(H$_2$O)$_2$]}$_n$	NFZ	1.934	0.35 μM	H$_2$O	37
	NFT	2.01	0.33 μM		
[In(dtztp)$_{0.5}$(OH)(H$_2$O)]·H$_2$O	NFT	6.26	7.4 ppm	H$_2$O	38
[Mg$_2$(APDA)$_2$(H$_2$O)$_3$]·5DMA·5H$_2$O	NFZ	9.0	108 ppb	DMF	39
	NFT	8.82	126 ppb		
[In$_2$(L)(OH)$_2$]·2DMF·2H$_2$O	NFZ	3.35	0.55 μM	DMF	40
[(CH$_3$)$_2$NH$_2$][TbZn$_3$(L)$_3$(HCOO)(H$_2$O)$_2$·5H$_2$O	NFT	183	39 ppb	H$_2$O	41
	NFZ	92.5	52 ppb		
{[Zn(BBDF)(ATP)]·2DMF·3H$_2$O}$_n$	NFT	4.65	0.098 μM	H$_2$O	**this work**
	NFZ	3.95	0.14 μM		

Note. NR: Not report

Table S6 Structure of 12 antibiotics

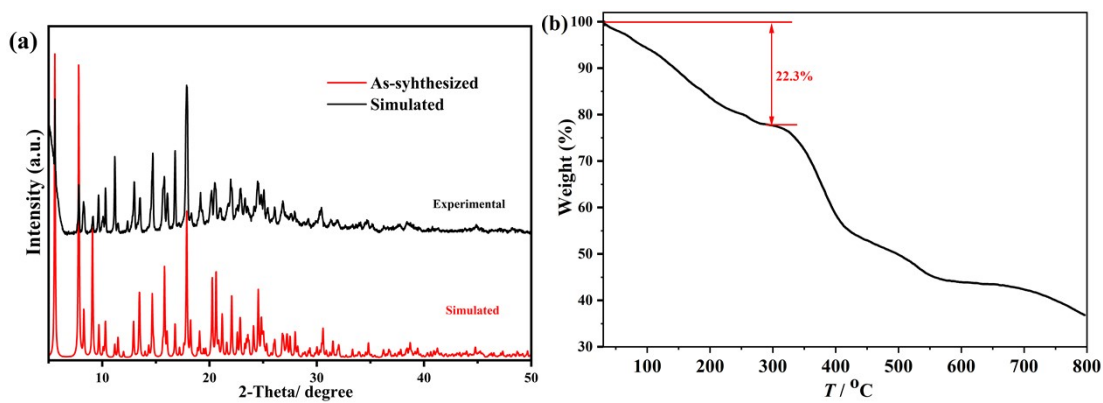| Name	Structure	Name	Structure
Nitrofurazone **NFZ**		Dimetridazole **DTZ**	
Nitrofurantoin **NFT**		Sulfadiazine **SDZ**	
Ornidazole **ODZ**		Sulfamethazine **SMZ**	
Ronidazole **RDZ**		Sulfathiazole **STZ**	
Metronidazole **MDZ**		Chloramphenicol **CAP**	
Ciprofloxacin **CPF**		Norfloxacin **NOF**	

Fig. S1 (a) The simulated and experimental PXRD patterns of **1**; (b) The TGA curve for **1** under N$_2$ atmosphere
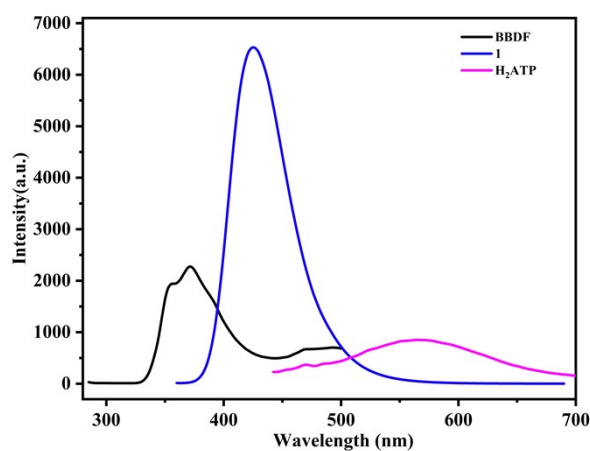

Fig. S2 Fluorescent emission spectra of free ligand BBDF and H$_2$ATP, as well as compound **1** in solid state at room temperature.
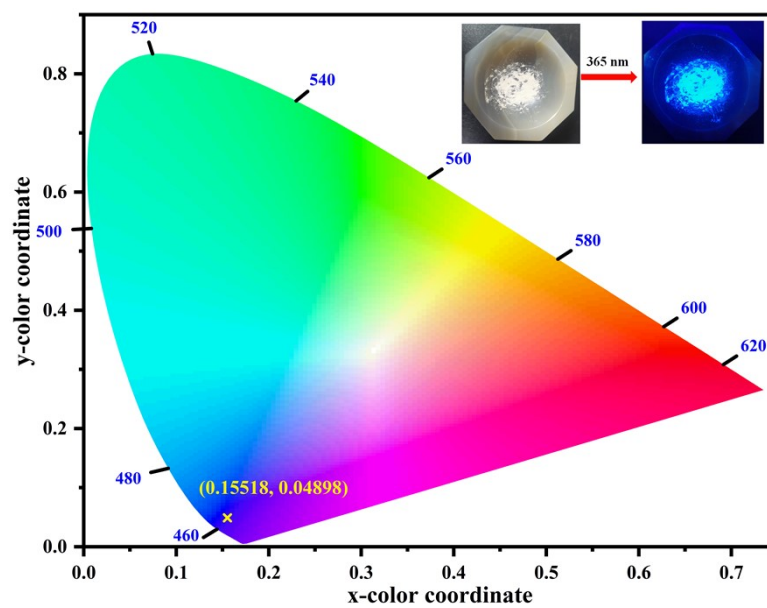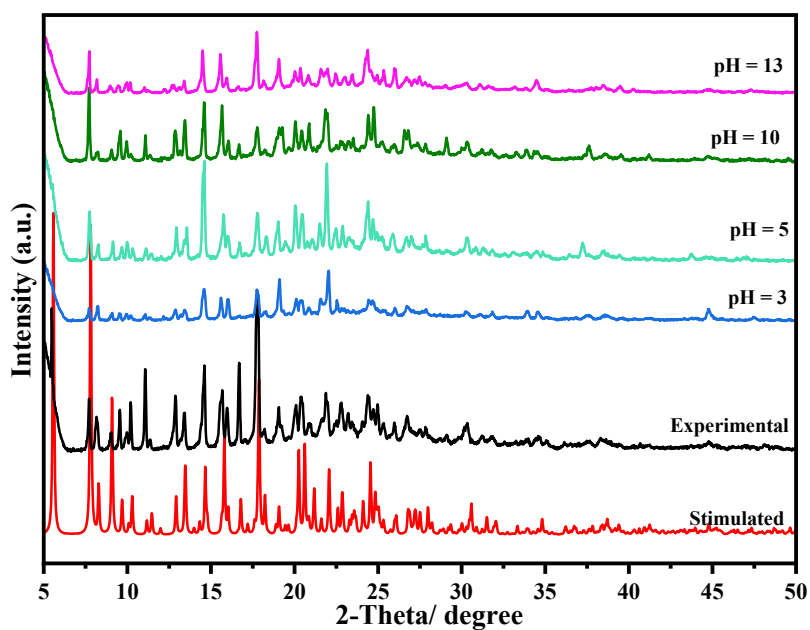

Figure S3 CIE coordinates of **1**

Fig. S4 The simulated and experimental PXRD patterns of **1** after immersing in aqueous solution with diverse pH values
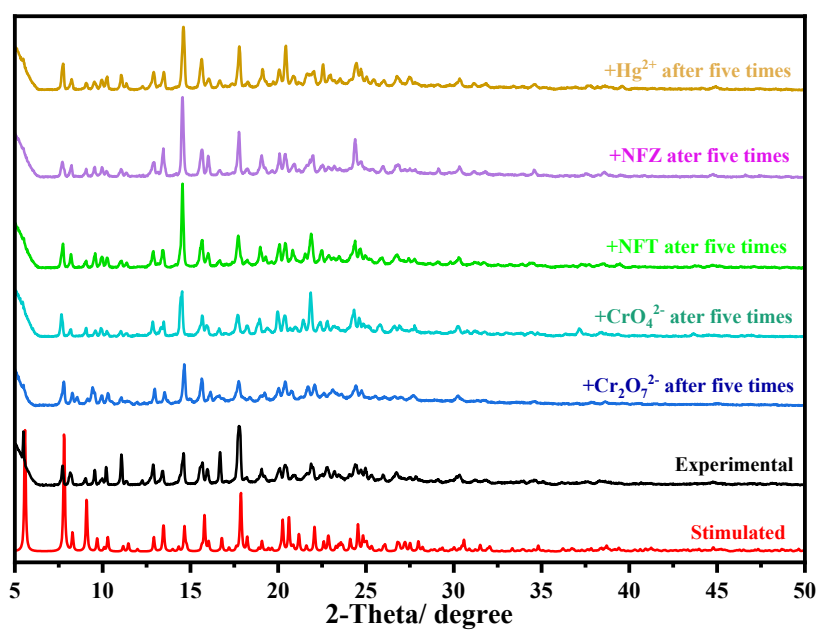

Fig. S5 The simulated and experimental PXRD patterns of **1** after sensing Hg^{2+}, $Cr_2O_7^{2-}$, CrO_4^{2-}, NFZ and NFT for 5 cycles
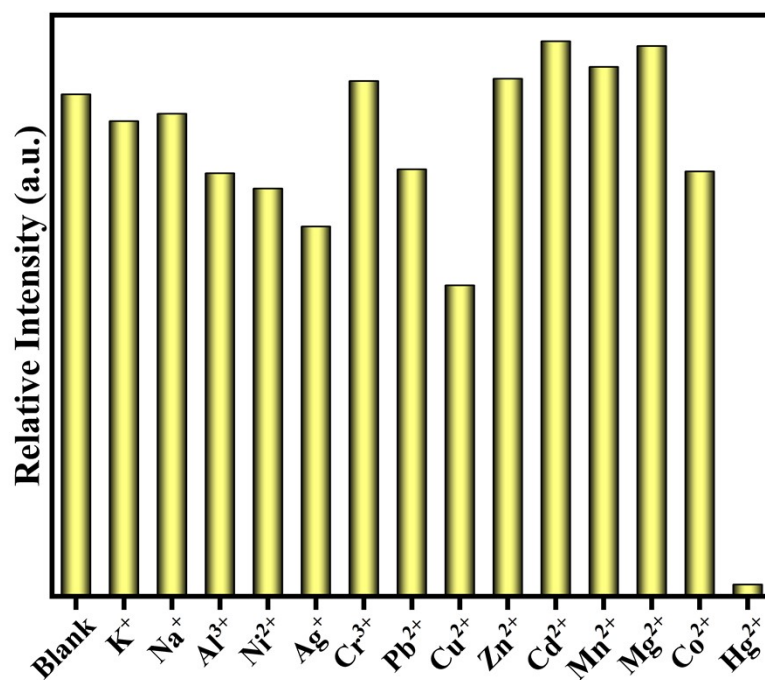
Fig. S6 Fluorescence Intensity of **1** in aqueous solution of different metal ion

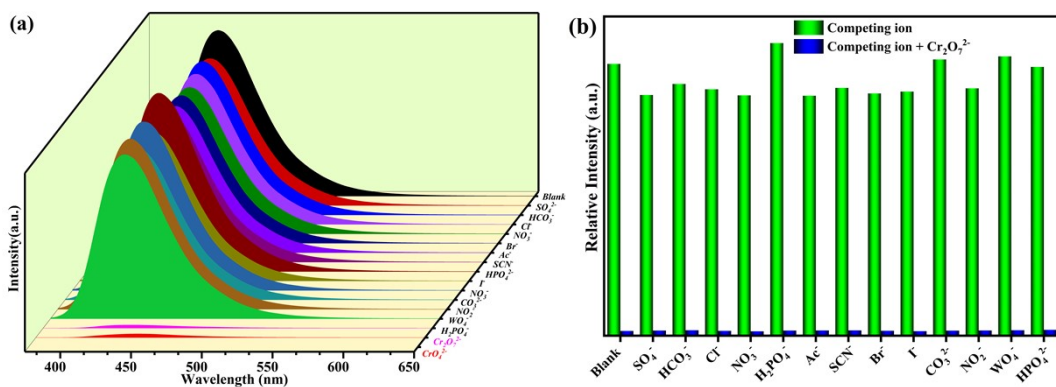**Fig. S7** (a) Fluorescence spectra of the suspension of **1** in different anions (b) Competitive experiments of **1** in sensing $Cr_2O_7^{2-}$ anion with the interference of other anion (0.5 mM) in H_2O solutions.
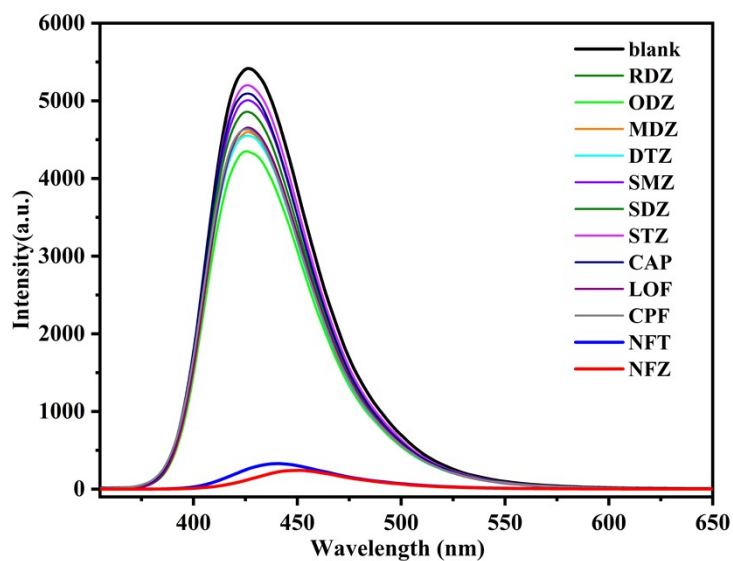
Fig. S8 Fluorescence spectra of the suspension of **1** in antibiotics compounds
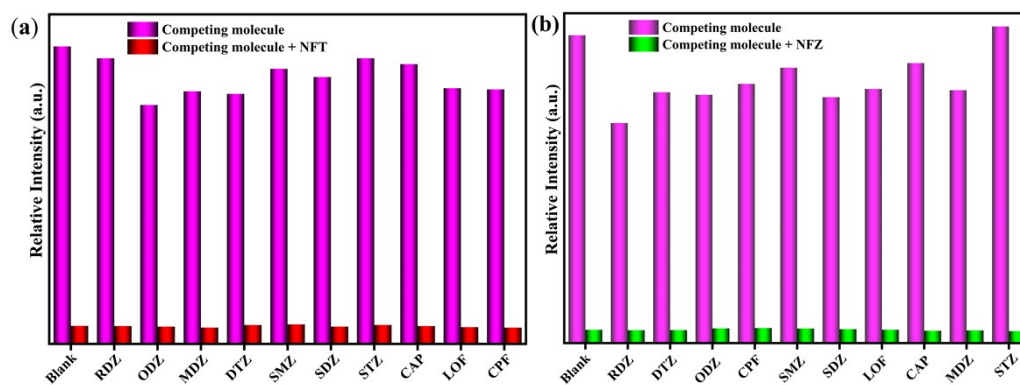
Fig. S9 Competitive experiments of **1** in sensing NFT (a) and NFZ (b) with the interference of other antibiotics compounds (0.2 mM) in H_2O solutions

Fig. S10 Luminescence response time of **1** after the addition of $Cr_2O_7^{2-}$ anion
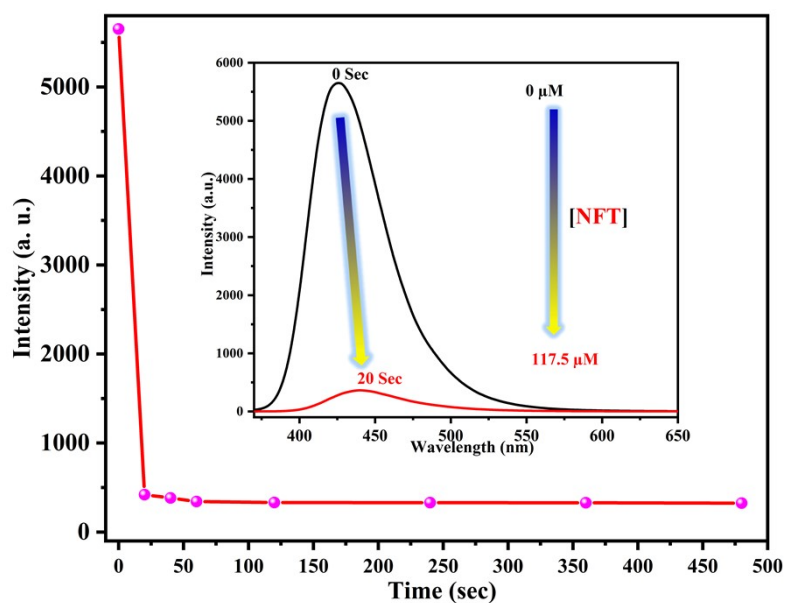
Fig. S11 Luminescence response time of **1** after the addition of NFT
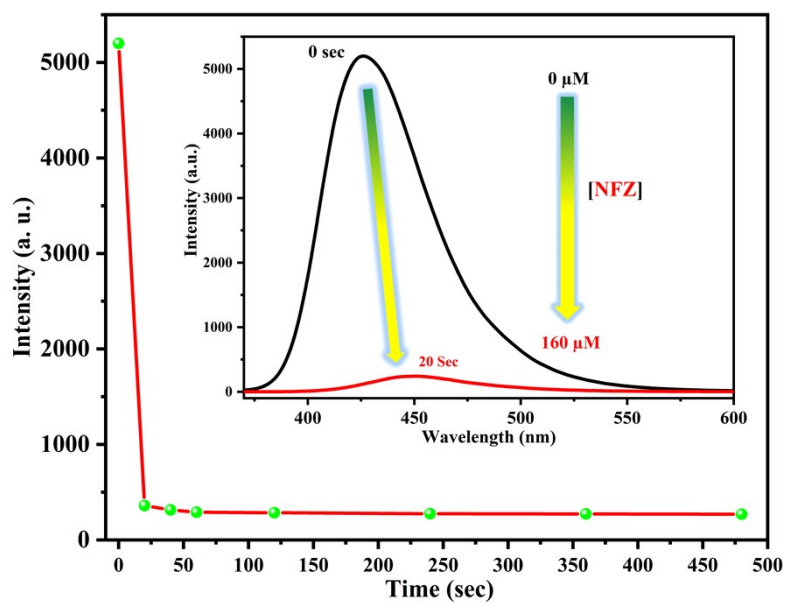
Fig. S12 Luminescence response time of **1** after the addition of NFZ
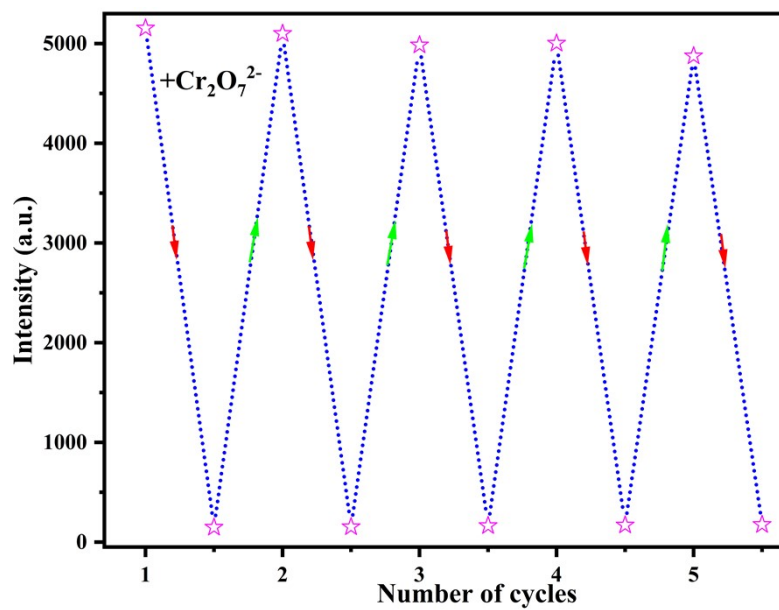
Fig. S13 Emission intensities of **1** toward $Cr_2O_7^{2-}$ after five cycles.
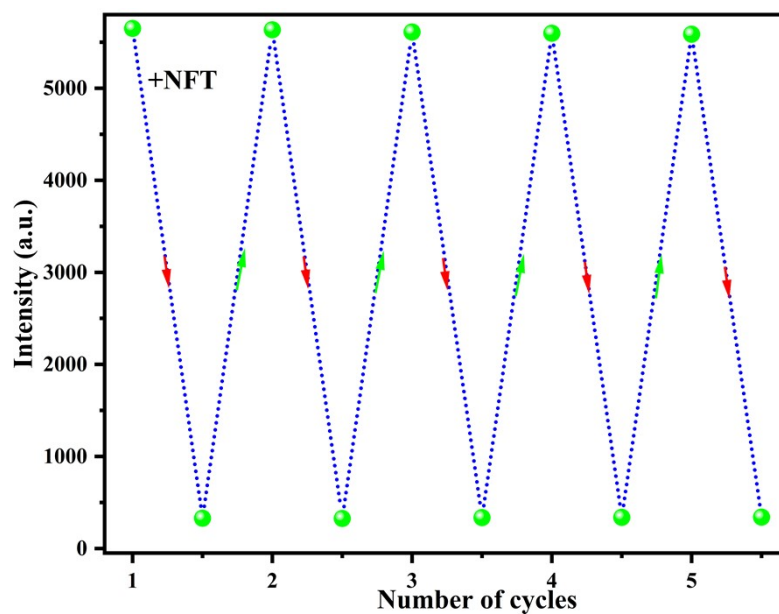
Fig. S14 Emission intensities of **1** toward NFT after five cycles.
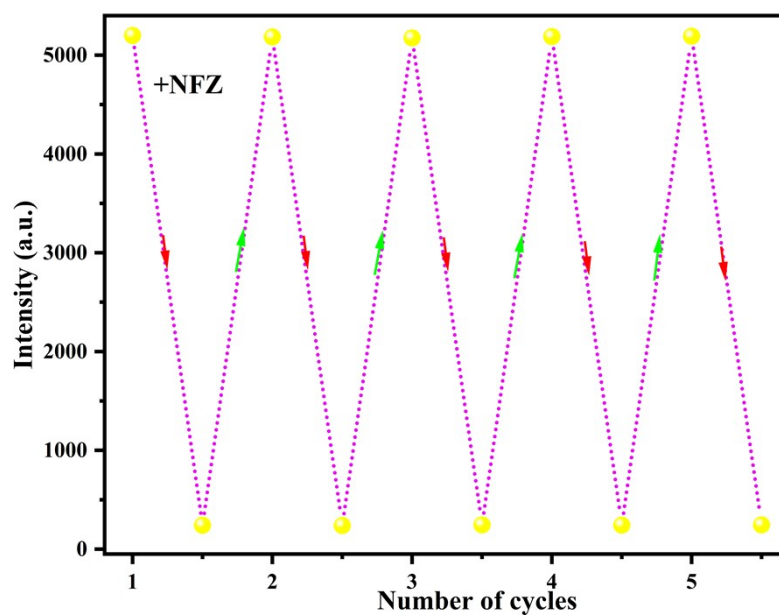
Fig. S15 Emission intensities of **1** toward NFZ after five cycles.
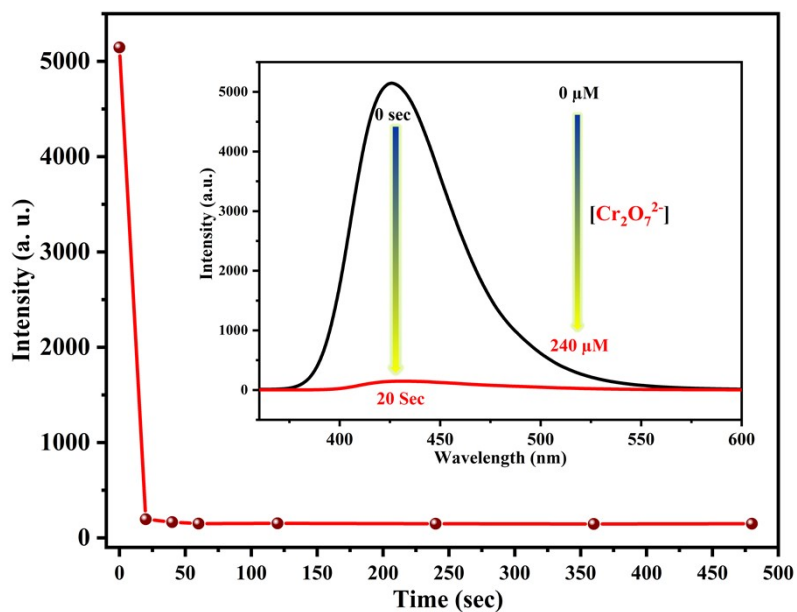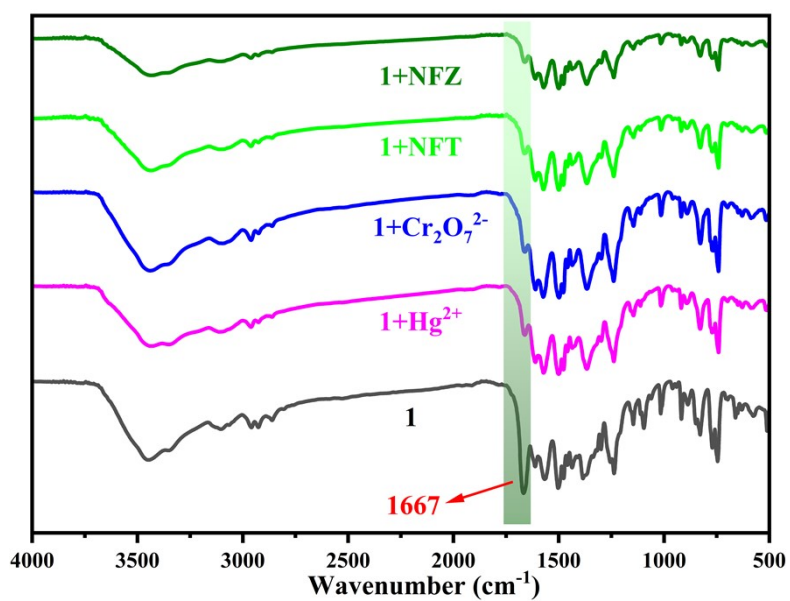

Fig. S16 IR spectra of **1** after sensing different analytes at room temperature. The intensity at the 1667 cm^{-1} absorption band reduced after being soaked in the H_2O solution, and the change in the IR spectra is due to the DMF molecules releasing from one dimensional (1D) channel.
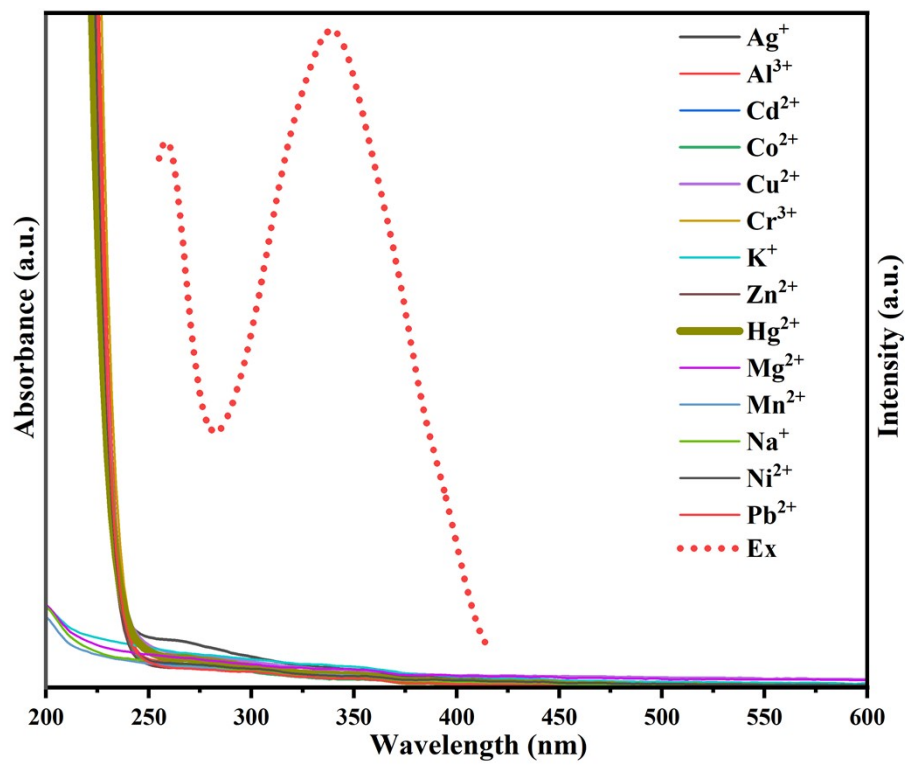
Fig. S17 The absorption spectra of cations and the excitation spectrum of **1**
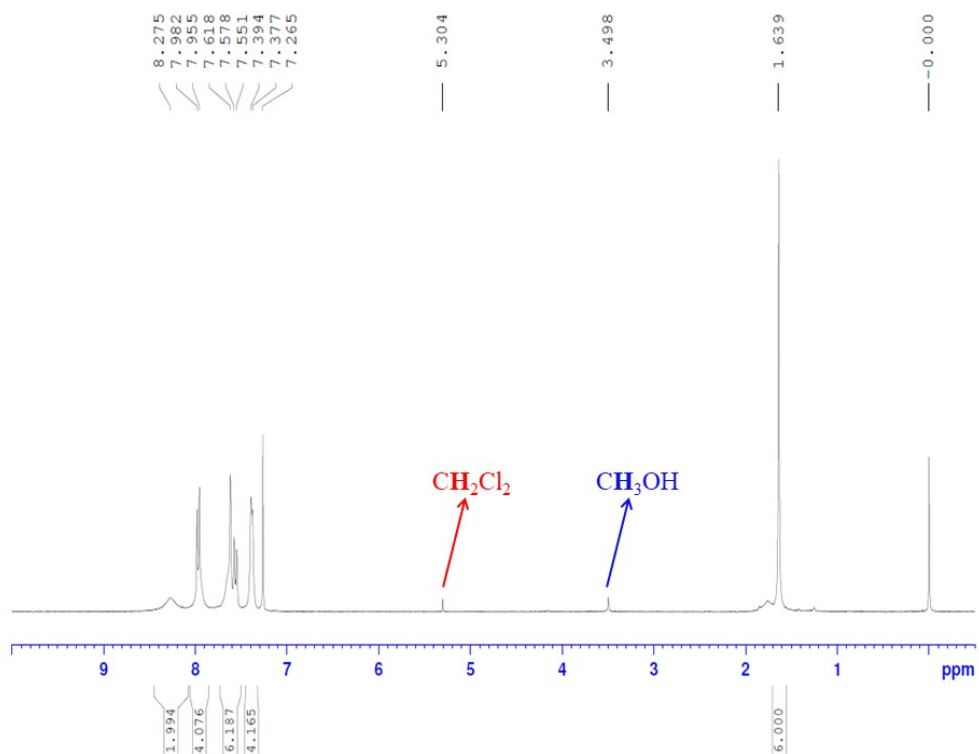
Fig. S18 ^{1}H NMR spectra of BBDF in CDCl$_3$
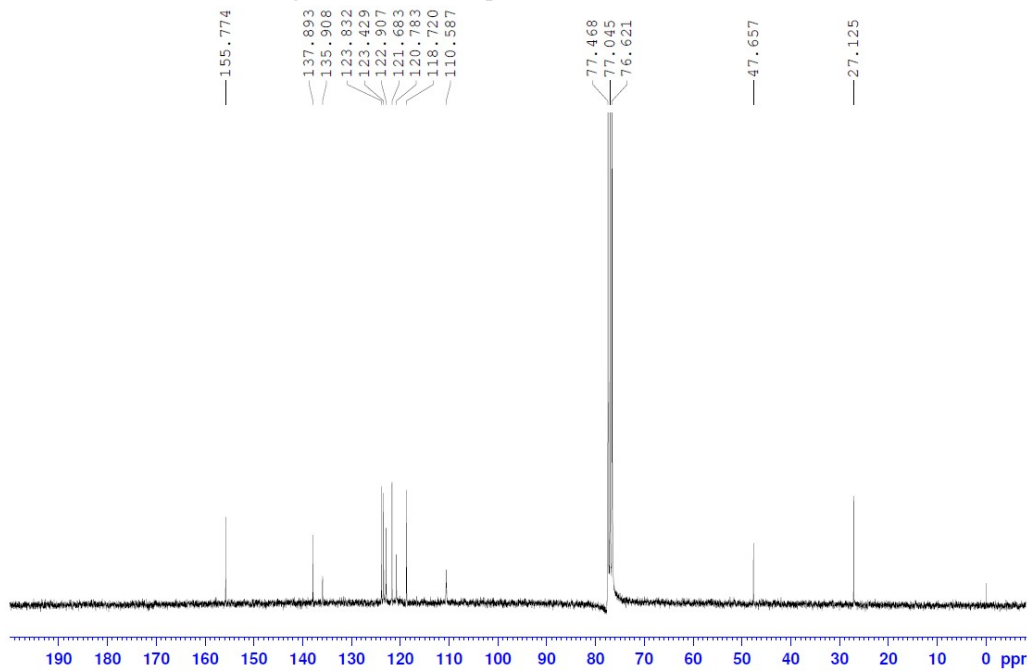
Fig. S19 ^{13}C NMR spectra of BBDF in CDCl$_3$

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