Novel 2D Isomorphic Lanthanide Complexes based on a bifunctional 5-(pyridin-3-yloxy)isophthalic acid: Synthesis, Structure, Fluorescence and Magnetic Properties

Wenwen Wei‡[a] *Xue Zhang*‡[a] *Liping Lu**[a] *Sisi Feng**[a,b]

[a]Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China, and [b]Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China.

‡ These authors contributed equally to this work and should be considered co-first authors

*Correspondence e-mail: luliping@sxu.edu.cn, ssfeng@sxu.edu.cn

Materials and Physical Measurements

All reagents and solvents used were commercially available and were used without further purification. H_2L(5-(pyridin-3-yloxy)isophthalic acid) was purchased from Jinan Trading Company (China). A Bruker TENSOR27 spectrometer was used to measure FT-IR, which was recorded with KBr pellets in the range of 4000-400 cm^{-1}. ^1H NMR spectrum was recorded on a Bruker AVANCE III spectrometer using the TMS as internal standard. All δ values are given in ppm. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer (Cu $K\alpha$ λ= 1.5418 Å) at a rate of 10° min^{-1} in the 2θ range of 5–50°. The thermogravimetric analysis was performed on a Dupont thermal analyzer between room temperature and 760 °C under an N_2 flow with a heating rate of 10 °C min^{-1}. The fluorescence spectra were measured on a Varian Cary Eclipse Fluoromax-4 spectrofluorometer with a xenon arc lamp as the light source. The Commission International del'Eclairage (CIE) color coordinates were calculated on the grounds of the international CIE standards. Quantum yields of luminescence measurements were carried out on the Edinburgh FS5 equipped with integrating sphere SC-30 in the wavelength range of 200 − 800 nm. Fluorescence lifetime was performed on an Edinburgh FLS980 luminescence spectrometer. Magnetic susceptibility data were obtained with a SQUID magnetometer (Quantum MPMS) in the temperature range 2.0–300 K by using an applied field of 1000 *Oe*.

X-ray crystallography

Crystallographic data of complexes **1-5** were collected on a Bruker D8-Quest diffractometer equipped with a Photon 100 detector, with a graphite monochromator Mo-Kα radiation (λ = 0.71073 Å) at room temperature. SADABS was applied for absorption corrections.[1] The structures of complexes **1-5** were solved by direct methods using the Olex2 program and refined on F^2 with the full-matrix least-squares technique using the SHELXL-2018 program.[2,3] After all the non-H atoms were refined, anisotropic thermal parameters and hydrogen atoms attached to the C atoms were added in ideal positions and refined by a riding model. H atoms attached to O atoms were located from difference Fourier maps and refined as riding in their as-found positions (O–H distances are approximately 0.82 Å), with U_{iso}(H) = 1.5U_{eq}(O). For complexes **1-5**, the PLATON/SQUEEZE program was used to remove the contributions of all disordered solvent molecules.[4] The full details of the solvent removed are included in the PLATON/SQUEEZE details section of the CIF. The stoichiometry of disordered water molecules in the overall formula is deduced through a combination of TGA. Crystal data and structure refinement details of complexes **1-5** are summarized in Table S1.

Table 1 Crystal data and structural refinement details for complexes **1**–**5**

Complex	**1**	**2**	**3**	**4**	**5**
Chemical formula	$C_{39}H_{29}Eu_2N_3O_{19}$	$C_{39}H_{29}Gd_2N_3O_{19}$	$C_{39}H_{29}N_3O_{19}Tb_2$	$C_{39}H_{29}Dy_2N_3O_{19}$	$C_{39}H_{29}Ho_2N_3O_{19}$
M_r	1147.57	1158.15	1161.49	1168.65	1173.51
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	296	296	296	296	296
a, b, c (Å)	15.9848 (10), 13.5213 (9), 19.9924 (14)	15.972 (1), 13.5069 (8), 19.9380 (12)	16.0024 (10), 13.5248 (8), 19.9626 (12)	15.9959 (10), 13.5136 (8), 19.9109 (12)	16.0071 (9), 13.5039 (8), 19.8981 (12)
β (°)	97.5038 (18)	97.696 (2)	97.450 (2)	97.597 (2)	97.694 (1)
V (Å^3)	4284.1 (5)	4262.5 (4)	4284.0 (5)	4266.2 (4)	4262.4 (4)

Z	4	4	4	4	4
μ (mm^{-1})	2.98	3.17	3.36	3.56	3.77
R_{int}	0.071	0.078	0.038	0.041	0.043
$R_1[F^2 > 2s(F^2)]$	0.046	0.044	0.028	0.032	0.030
$wR_2(F^2)$	0.080	0.076	0.065	0.073	0.061
GOF	1.02	1.02	1.01	1.01	0.99

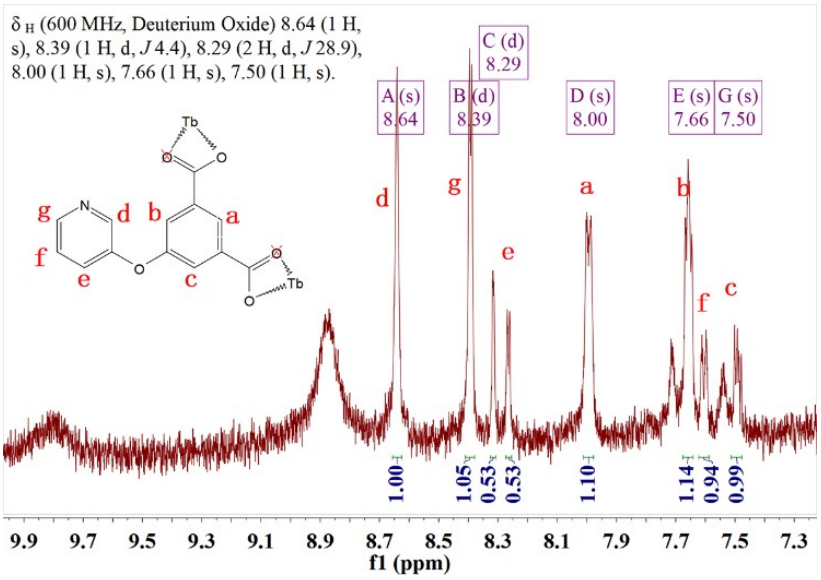

Figure S1 ^{1}H NMR of complex **3** in D_2O.

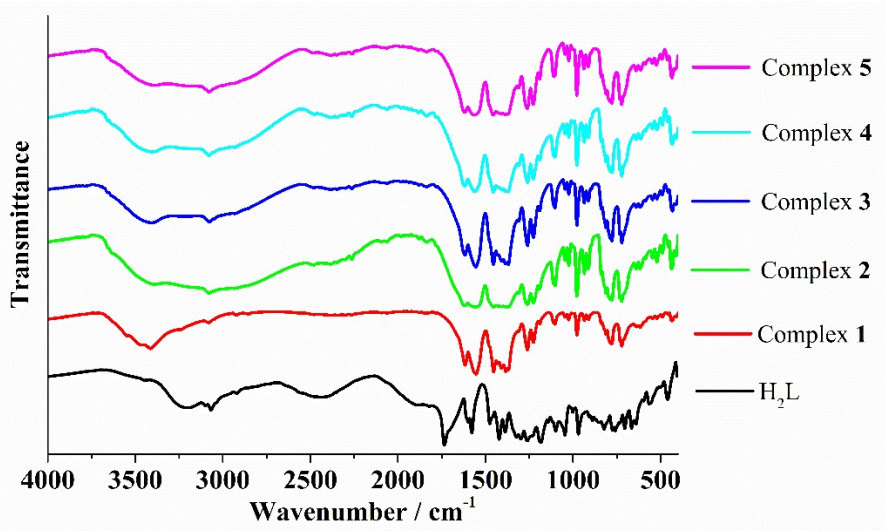

Fig. S2 IR spectra of complexes **1**–**5**.

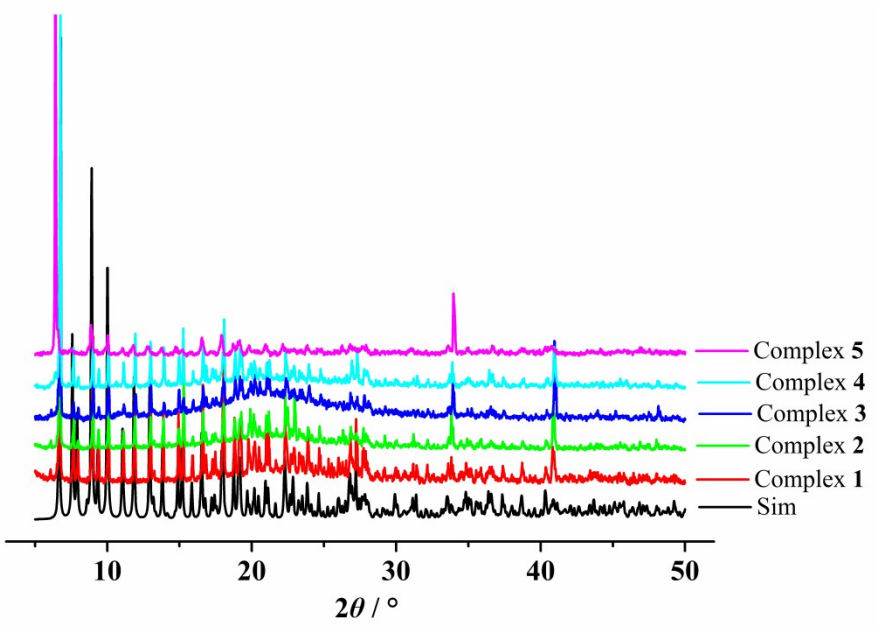

Fig. S3 PXRD patterns of complexes **1**–**5**.

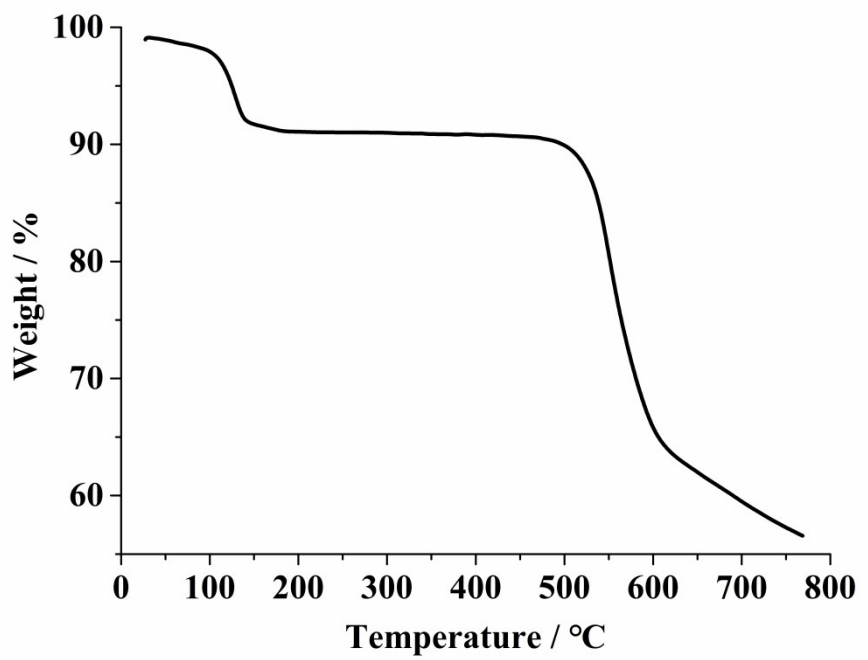

Fig. S4 The thermal curve of complex **3**.

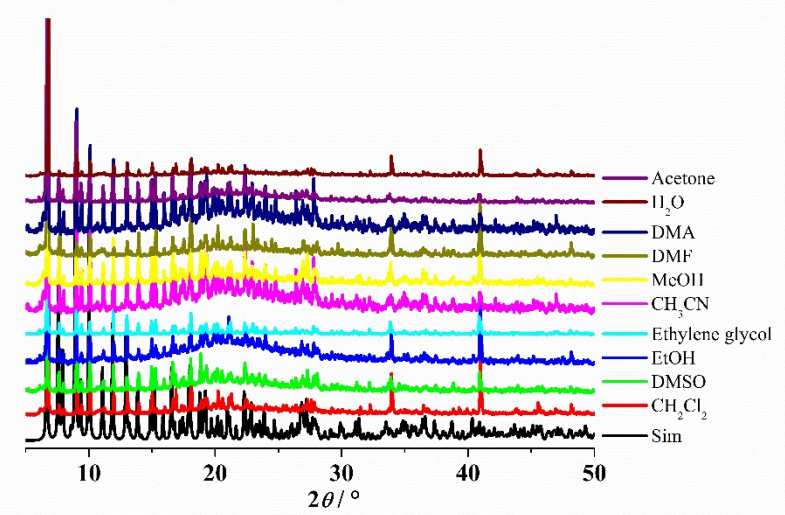

Fig. S5 The PXRD patterns of **3** after being soaked in different solvents.

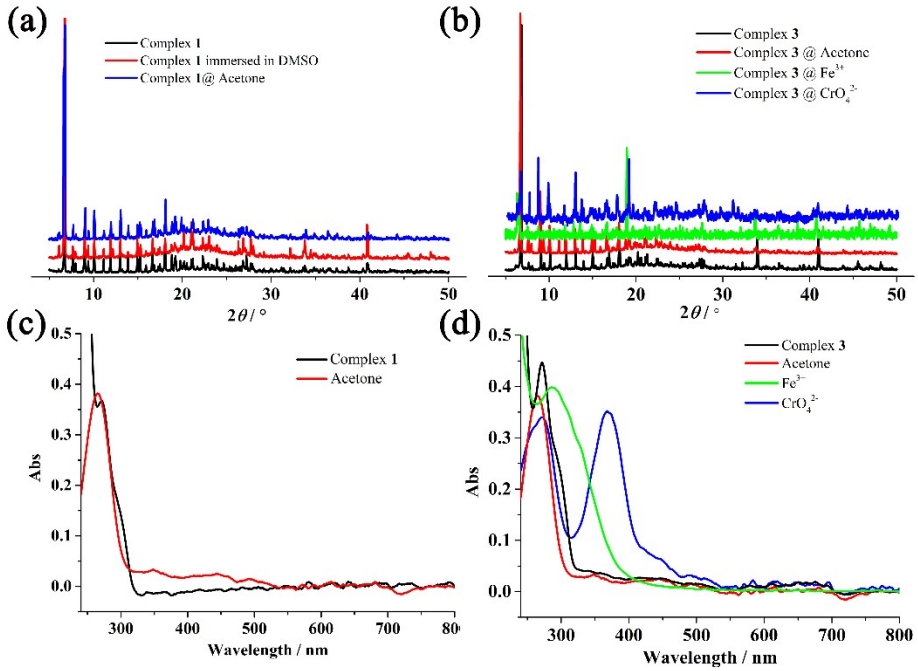

Fig. S6 (a) PXRD patterns of **1** before and after immersed in DMSO and acetone for three days; (b) PXRD patterns of complex **3** before and after immersed in acetone, Fe^{3+} and CrO_4^{2-} for three days; (c) UV-Vis spectra of acetone and complex **1** in DMSO; (d) UV-Vis spectra of acetone, complex **3**, Fe^{3+} and CrO_4^{2-} in water.

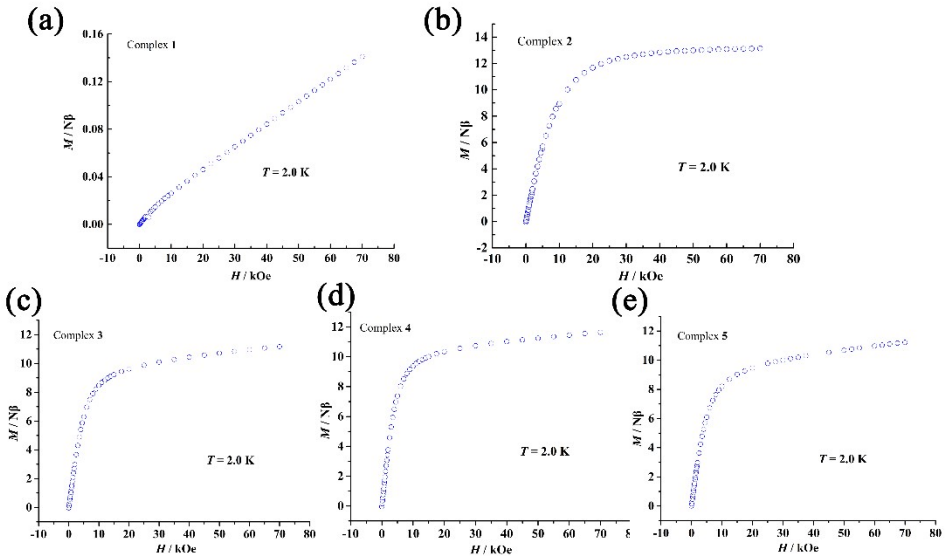

Fig. S7 M and H plot at 2 K for complexes **1**-**5**.

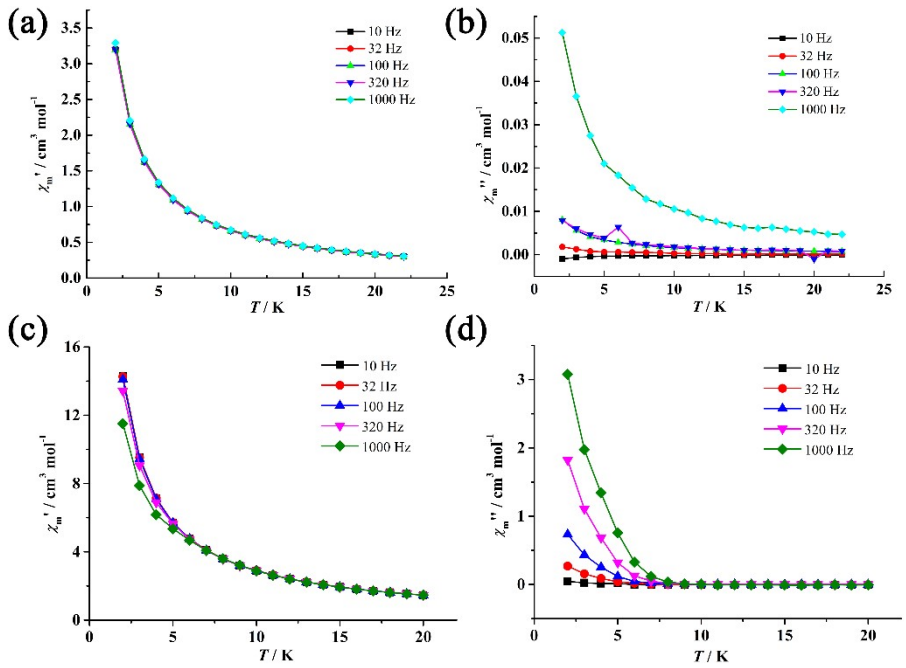

Fig. S8 Temperature dependences of χ_m' and χ_m'' for complexes **2** and **4** under different frequencies.

Table S2 A summary of properties of fluorescent probes based on complexes for sensing of acetone

Complex	Analyte	LOD (M)	Media	Ref.
$[Zn_2(H_2BCA)_2(o\text{-}bimb)_2(H_2O)_2]_n$	acetone	9.00×10^{-8}	H_2O	5
$\{[Zn(H_2BCA)(m\text{-}bib)]\cdot H_2O\}_n$	acetone	1.30×10^{-7}	H_2O	5
ZIF-8	acetone	1.10×10^{-6}	H_2O	6
$[Tb_2(\mu_3\text{-}L)_2(\mu_4\text{-}L)(H_2O)_3]_n\cdot nH_2O$	acetone	2.08×10^{-6}	H_2O	This work

$SmFeO_3$	acetone	2.60×10^{-6}	H_2O	7
$[Cu(dmpy)_3(H_2O)_2](H_2O)(ClO_4)_2$	acetone	1.78×10^{-5}	CH_3CN	8
$ZnO–In_2O_3$	acetone	4.3×10^{-5}	H_2O	9
$LnFeO_3$	acetone	2.04×10^{-4}	H_2O	10
$NdFeO_3$	acetone	3.0×10^{-4}	H_2O	11
$[Eu_2(\mu_3\text{-L})_2(\mu_4\text{-L})(H_2O)_3]_n\cdot nH_2O$	acetone	3.59×10^{-4}	DMSO	This work

Table S3 A summary of properties of fluorescent probes based on complexes for sensing of Fe^{3+} ions

Complex	Analyte	K_{SV} (M^{-1})	LOD (M)	Media	Ref.
GTGU-1 (Tb)	Fe^{3+}	1.88×10^{6}	1.0×10^{-9}	H_2O	12
$[Tb_2(\mu_3\text{-L})_2(\mu_4\text{-L})(H_2O)_3]_n\cdot nH_2O$	Fe^{3+}	6.85×10^{5}	4.8×10^{-8}	H_2O	This work
$\{[Cd_4L_2]\cdot 1,4\text{-bmib}\}_n$	Fe^{3+}	1.15×10^{5}	2.6×10^{-7}	H_2O	13
Eu^{3+}@MIL-124	Fe^{3+}	3.87×10^{4}	2.8×10^{-7}	H_2O	14
Tb-MOF	Fe^{3+}	1.63×10^{5}	3.5×10^{-7}	DMF	15
$[Cd_4L_2(1,4\text{-bimb})_3]_n$	Fe^{3+}	8.54×10^{4}	3.5×10^{-7}	H_2O	13
Tb-MOF	Fe^{3+}	1.28×10^{4}	5.0×10^{-7}	H_2O	16
JLU-MOF71	Fe^{3+}	5.77×10^{4}	6.4×10^{-7}	DMF	17
$Tb(\mu_6\text{-}H_2\text{cpboda})(\mu_2\text{-}OH_2)_2]\cdot xH_2O]_n$	Fe^{3+}	5.50×10^{4}	8.4×10^{-7}	H_2O	18
Eu-CP	Fe^{3+}	1.03×10^{5}	9.4×10^{-7}	H_2O	19
Tb-CP	Fe^{3+}	1.91×10^{5}	1.1×10^{-6}	H_2O	19
Tb-MOF-A	Fe^{3+}	4.04×10^{4}	1.3×10^{-5}	H_2O	20

Table S4 A summary of properties of fluorescent probes based on complexes for sensing of CrO_4^{2-} anions

Complex	Analyte	K_{SV} (M^{-1})	LOD (M)	Media	Ref.
TMU-41(OMS)	CrO_4^{2-}	1.0×10^{6}	2.0×10^{-8}	H_2O	21
Y(BTC)(DMF):0.1Eu	CrO_4^{2-}	1.18×10^{3}	3.0×10^{-8}	H_2O	22
$Tb(\mu_6\text{-}H_2\text{cpboda})(\mu_2\text{-}OH_2)_2]\cdot xH_2O]_n$	CrO_4^{2-}	8.11×10^{5}	4.06×10^{-8}	H_2O	This work
NUM-5	CrO_4^{2-}	1.24×10^{5}	3.0×10^{-7}	H_2O	23
SQDs@UiO-66-NH_2	CrO_4^{2-}	2.92×10^{4}	1.70×10^{-7}	H_2O	24
$[Zn(OBA)_2(L1)\cdot 2DMA]_n$	CrO_4^{2-}	1.16×10^{4}	3.84×10^{-6}	H_2O	25
$[Tb(Hmcd)(H_2O)(DMF)_2]_n$	CrO_4^{2-}	9.30×10^{2}	3.88×10^{-5}	DMF	26
$[Eu(Hmcd)(H_2O)(DMF)_2]_n$	CrO_4^{2-}	1.65×10^{2}	2.37×10^{-4}	DMF	26

References

1 G. M. Sheldrick, SADABS: *Empirical Absorption Correction Program*, University of Gottingen, Gottingen, Germany, 1997.

2 G. M. Sheldrick, *Acta Cryst*., 2015, **C71**, 3–8.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl.*

Crystallogr. 2009, **42**, 339−341.
4 A. L. Spek and A. Platon, *Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2006.
5 X. T. Zhang, H. C. Chen, B. Li, G. Z. Liu, X. Z. Liu, *CrystEngComm*, 2019, **21**, 1231-1241.
6 F. A. Bahos, A. S. Vidal, C. S. Pérez, J. M. Saniger, I. Gràcia, M. M. S. Alba, D. Matatagui, *Biosensors*, 2019, **9**, 4.
7 T. Chen, Z. L. Zhou, Y. D. Wang, *Sens. Actuators B. Chem*, 2009, **143**, 124-131.
8 M. Muddassir, A. Alarifi, M. Afzal, K. A. Alshali, N. A. Y. Abduh, A. Beagan, *RSC Adv*, 2020, **10**, 42137-42146.
9 X. Chi, C. B. Liu, Y. Li, H. Y. Li, L. Liu, X.Q. Bo, L. L. Liu, C. Su, *Mat. Sci. Semicon Proc*., 2014, **27**, 494-499.
10 X. C. Liu, H. M. Ji, Y. F. Gu, M. X. Xu, *Mater Sci. Eng. B*, 2006, **133**, 98-101.
11 Z. L. Wu, R. Zhang, M. Zhao, S. M. Fang, Z. X. Han, J. F. Hu, K. Y. Wang, Int. *J. Miner. Metall. Mater*., 2012, **19**, 141-145.
12 M. L. Han, G. W. Xu, D. S. Li, M. L. Azofra, J. Zhao, B. Chen and C. Sun, *ChemistrySelect*, 2016, **1**, 3555–3561.
13 B. Zhu, C. B. Fan, C. G. Xu, L. L. Wang, C. F. Bi, X. Zhang and Y. H. Fan, *Microchemical Journal* 2021, **162**, 105880.
14 X. Y. Xu and B. Yan, *ACS Appl. Mater. Interfaces*, 2015, **7**, 721–729.
15 Y. M. Zhao, X. Zhai, L. Shao, L. L. Li, Y. L. Liu, X. M. Zhang, J. H. Liu, F. B. Meng and Y. Fu, *J. Mater. Chem. C*, 2021, **9**, 15840–15847.
16 J. X. Li, B. Q. Yu, L. H. Fan, L. Wang, Y. C. Zhao, C. Y. Sun, W. J. Li and Z. D. Chang, *Journal of Solid State Chemistry*, 2022, **306**, 122782.
17 C. Y. Yu, X. D. Sun, L. F. Zou, G. H. Li, L. R. Zhang and Y. L. Liu, *Inorg. Chem*. 2019, **58**, 4026−403.
18 D. D. Yang, L. P. Lu, S. S. Feng and M. L. Zhu, *Dalton Trans*., 2020, **49**, 7514-7524.
19 W. Gao, A. M. Zhou, H. Wei, C. L. Wang, J. P. Liu and X. M. Zhang, *New J. Chem*., 2020, **44**, 6747-6759.
20 H. H. Yu, J. Q. Chi, Z. M. Su, X. Li, J. Sun, C. Zhou,X. L. Hu and Q. Liu, *CrystEngComm*, 2020, **22**, 3638–3643.
21 N. Abdollahi, A. Morsali, *Anal Chim Acta*, 2019, **1064**, 119-125.
22 T. W. Duan, B. Yan, H. Weng, *Micropor. Mesopor. Mat*., 2015, **217**, 196-202.
23 M. Knies, M.Kaiser, A. Lsaeva, U. Muller, T. Doert, M. Ruck, *Chem. Eur. J*, 2018, **24**, 1-8.
24 Y. Q. Zhang, J. X. Liu, X. H. Wu, W. Q. Tao, Z. Li, *Anal Chim Acta*, 2020, **1131**, 68-79.
25 B. W. Qin, X. Y. Zhang, J. J. Qiu, G. Gahungu, H. Y. Yuan, J. P. Zhang, *Inorg. Chem*, 2021, **60**, 1716-1725.
26 X. Li, J. X. Tang, H. Liu, K. Gao, X. G. Meng, J. Wu, H. W. Hou, *Chem. Asian J*. 2019, **14**, 3721-3727.