Electronic Supplementary Information

Two Anthracene-based Metal-Organic Frameworks for Highly Effective Photodegradation and Luminescent Detection in Water

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SI. Supporting Figures

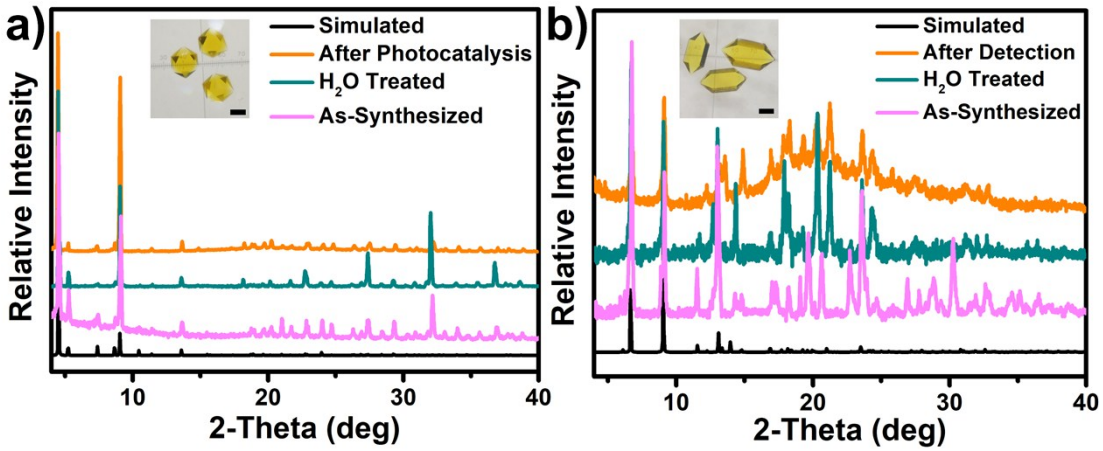

Fig. S1 Powder X-ray diffraction (PXRD) patterns of a) **Eu-ADBA** and b) **In-ADBA**. Inset: the single crystal image, scale bar: 200 μm.

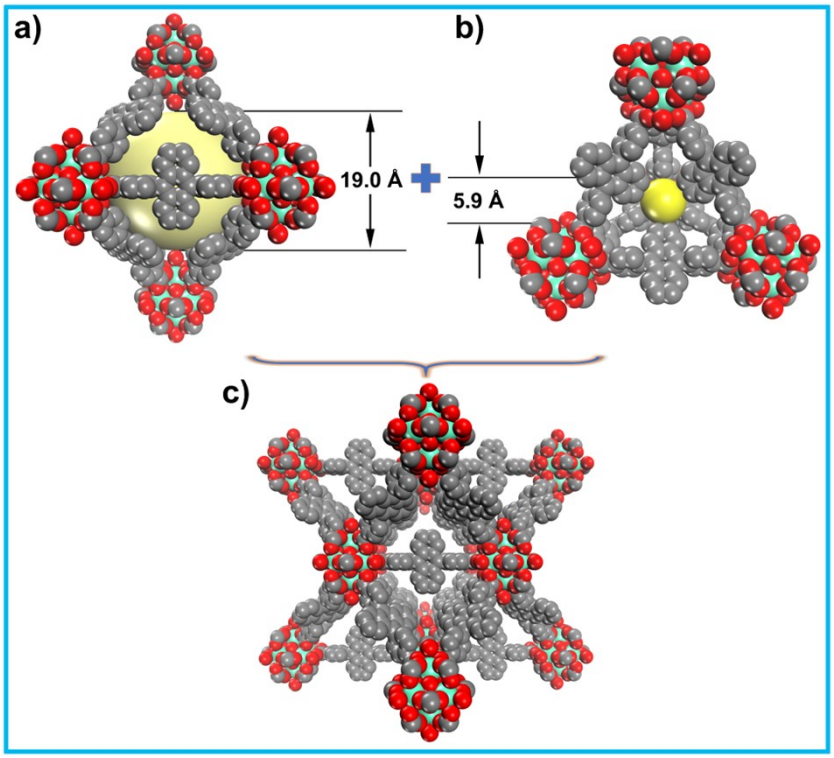

Fig. S2 CPK views of structure of **Eu-ADBA**: a) octahedral cage with diameter of 19.0 Å, b) tetrahedral cage with diameter of 5.9 Å, c) unit cell.

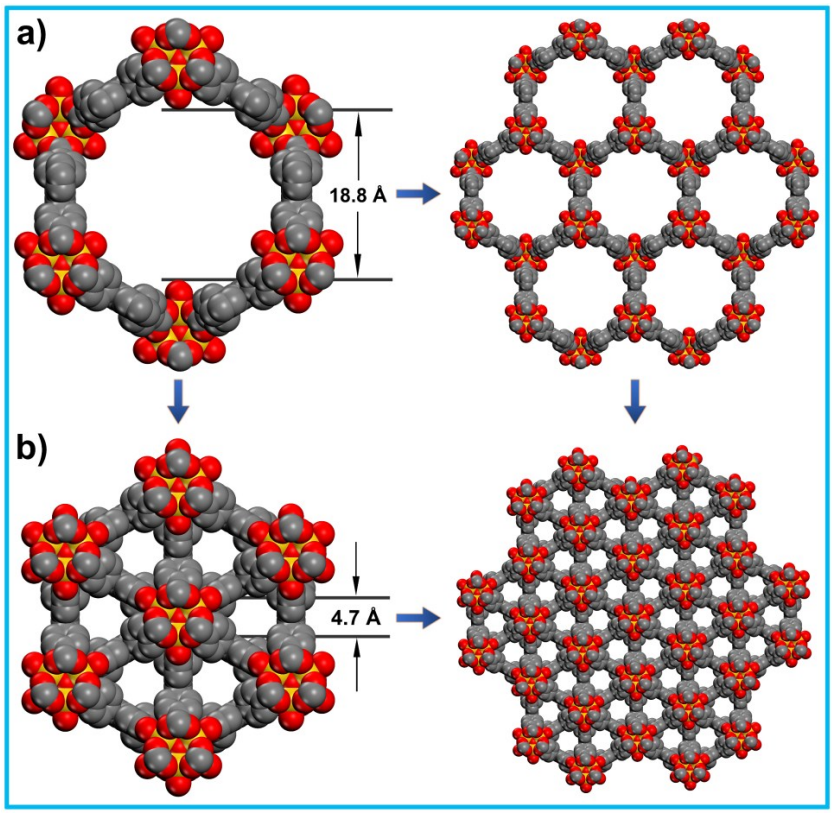

Fig. S3 CPK views of structure of **In-ADBA**: a) non-folded network with hexagon channel with diameter of 18.8 Å, b) 3-folded network with triangular channel with diameter of 4.7 Å.

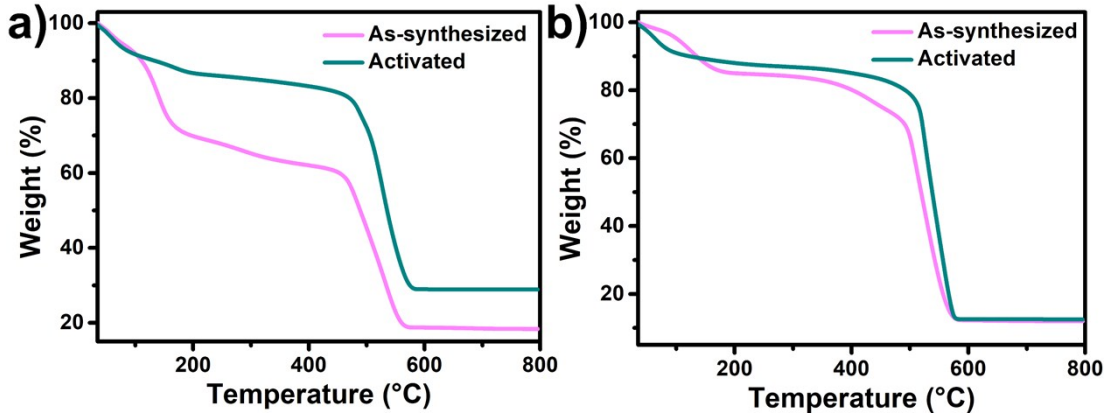

Fig. S4 TGA curves of a) **Eu-ADBA** and b) **In-ADBA**.

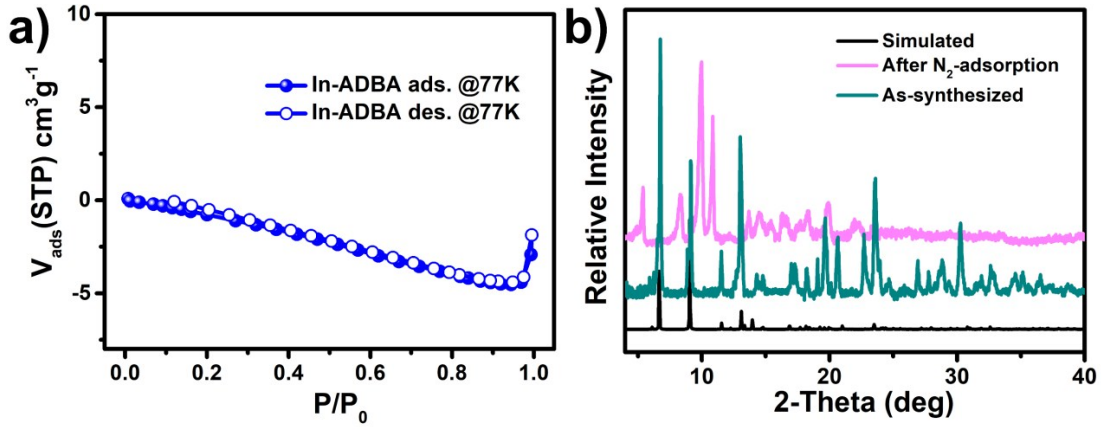

Fig. S5 a) N_2 sorption isotherm at 77 K under 1 bar of **In-ADBA**, b) PXRD patterns of **In-ADBA**.

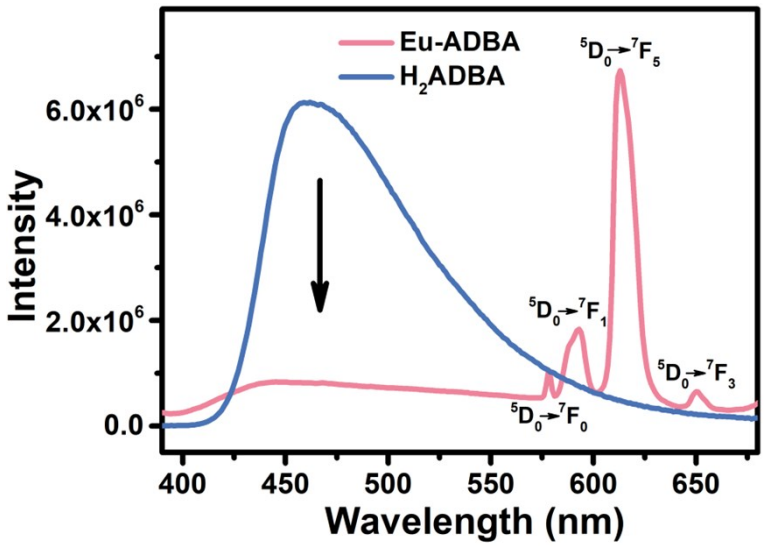

Fig. S6 Solid-state photoluminescent spectra of **Eu-ADBA** and free H_2ADBA ligand excited at 350 nm at room temperature.

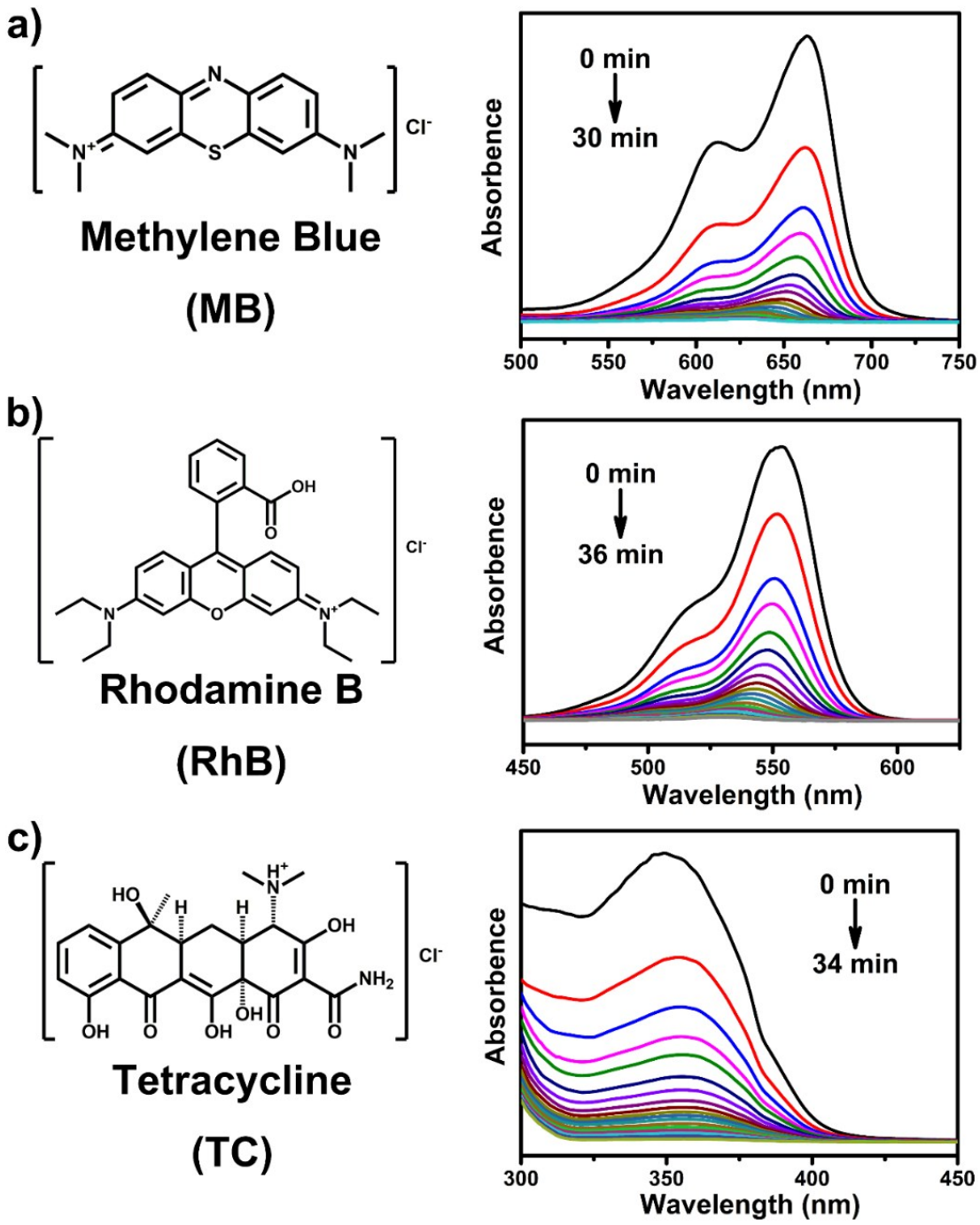

Fig. S7 Structural formula and time-dependent liquid-state UV-vis spectra of photodegradation of a) MB, b) RhB and c) TC using **Eu-ADBA**.

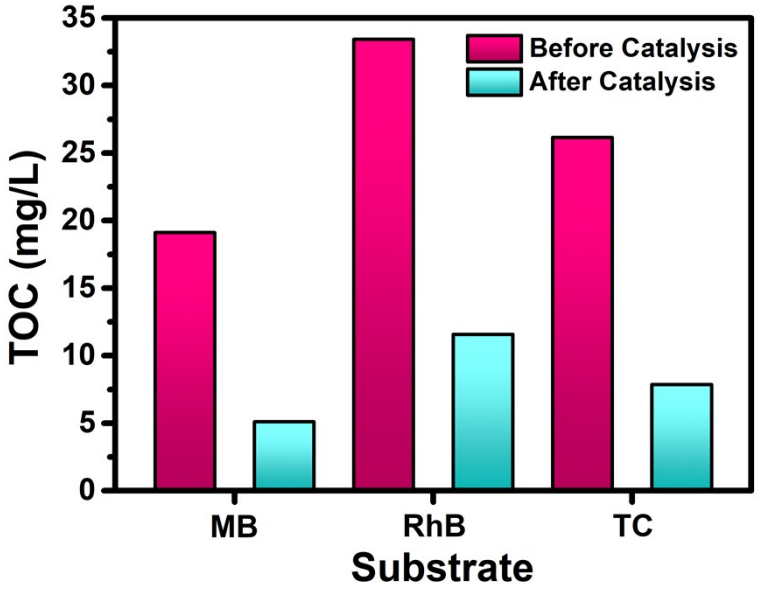

Fig. S8 TOC test of photodegradation using **Eu-ADBA**.

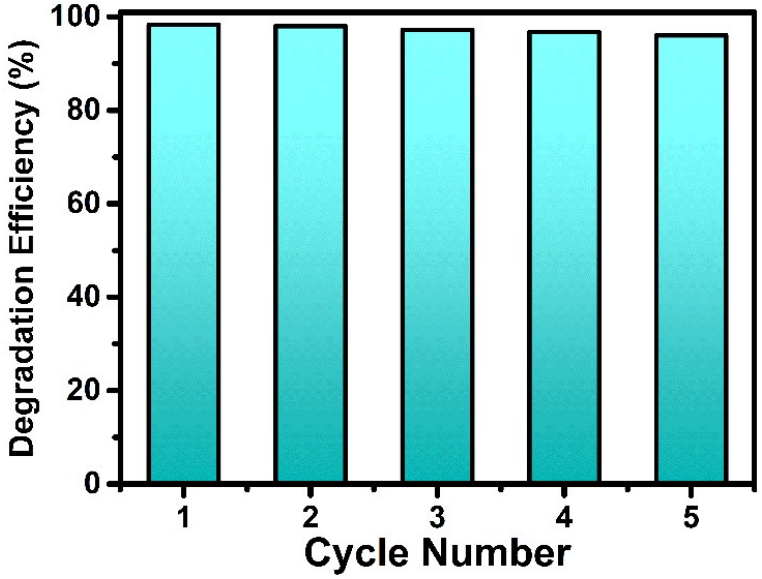

Fig. S9 Cyclic test of photocatalytic degradation of RhB using **Eu-ADBA**.

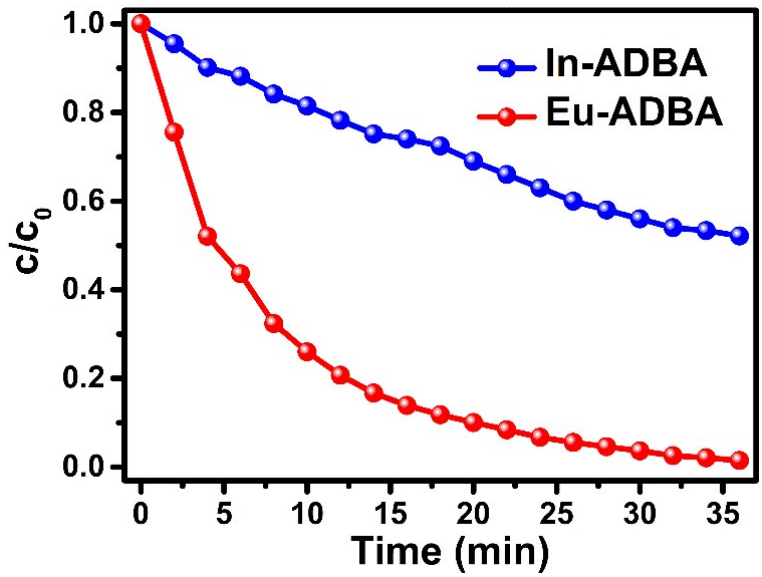

Fig. S10 Comparison of photocatalytic activities between **Eu-ADBA** and **In-ADBA**.

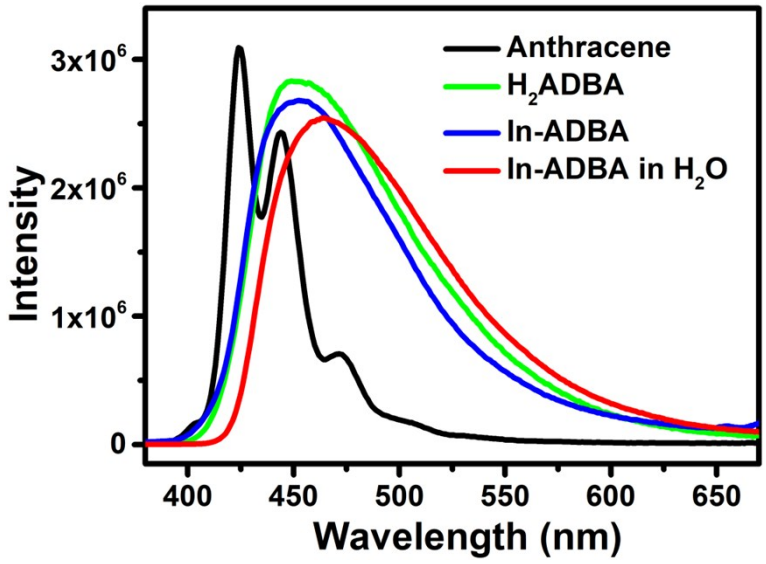

Fig. S11 Photoluminescent spectra of free anthracene molecules, free H_2ADBA ligand, **In-ADBA** and **In-ADBA** dispersed in water excited at 350nm.

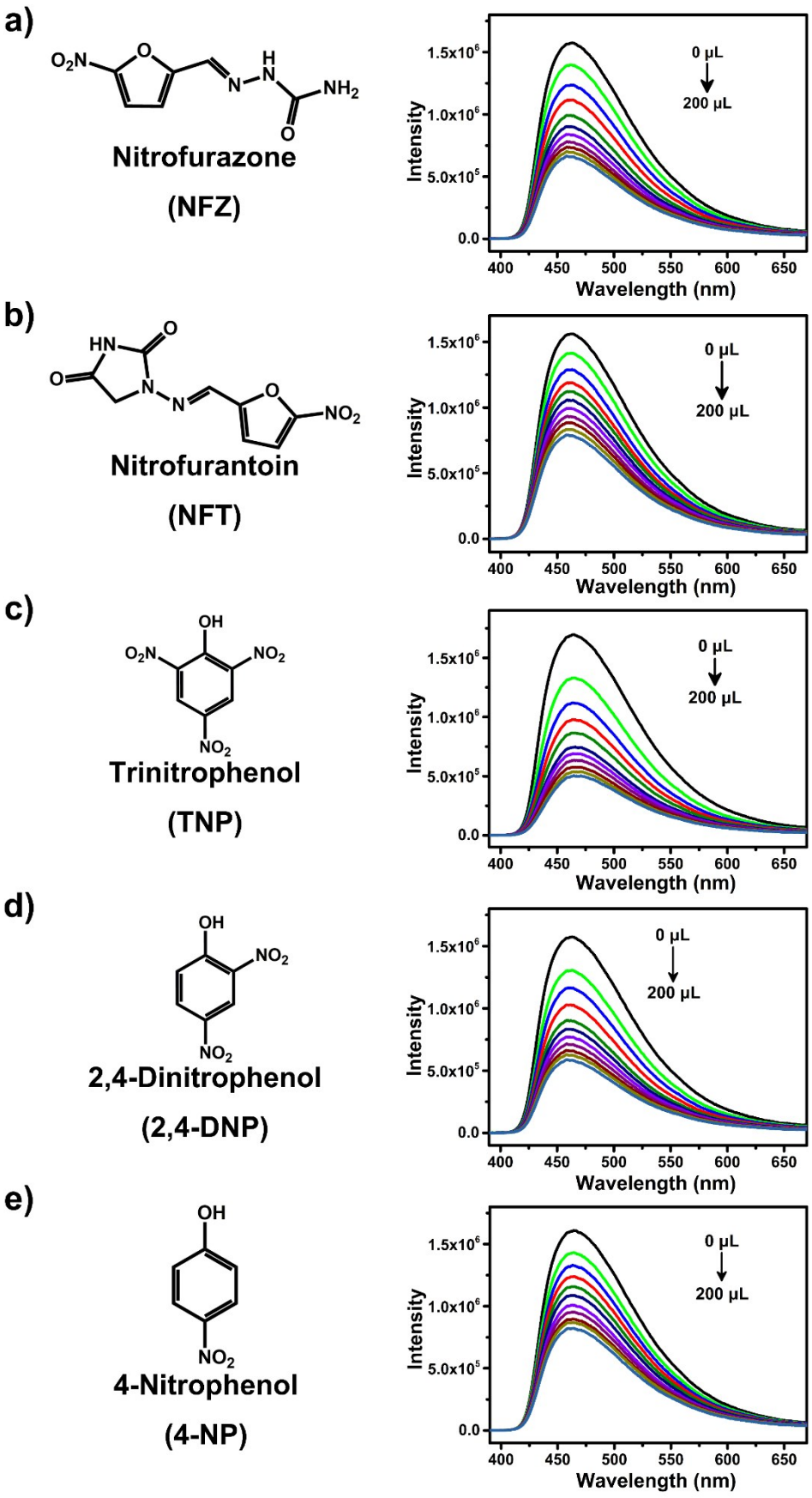

Fig. S12 Structural formula and luminescence spectra of low-consentration titrations of a) NFZ, b) NFT, c) TNP, d) 2,4-DNP and e) 4-NP using **In-ADBA**.

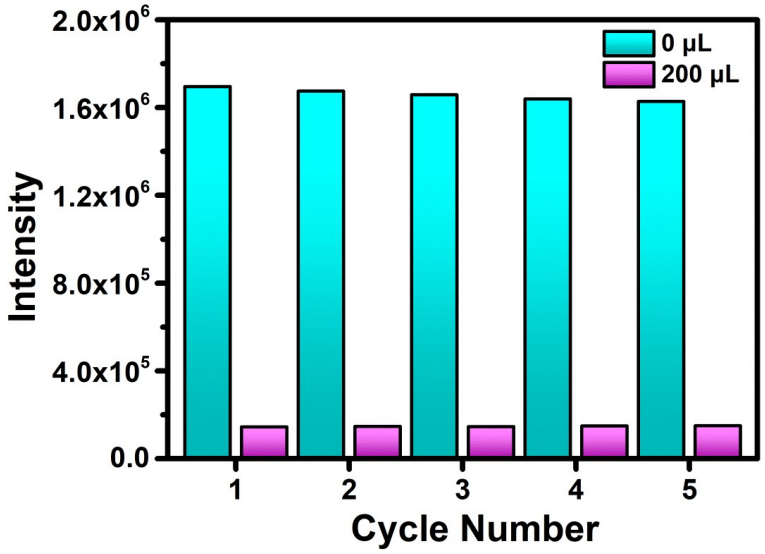

Fig. S13 Cyclic detection of TNP using **In-ADBA**.

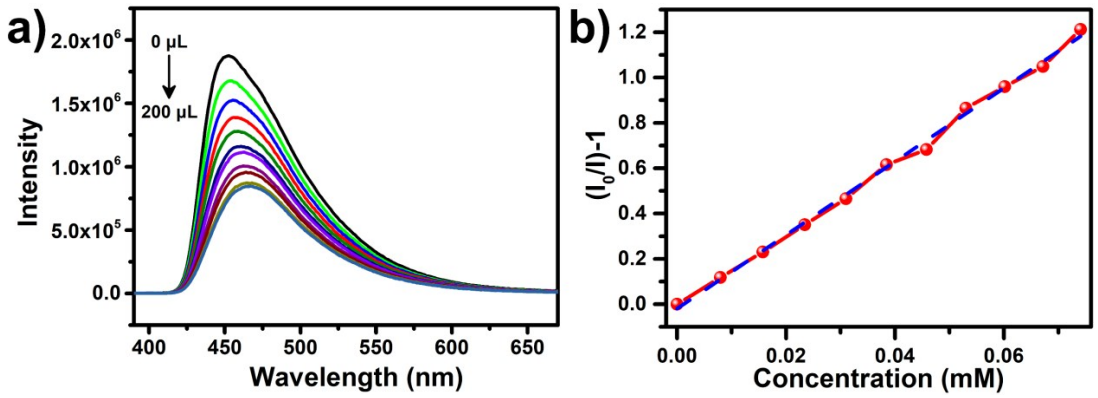

Fig. S14 a) Luminescence spectra of fluorescence-quenching titrations of TNP using H_2ADBA, b) K_{SV} plot.

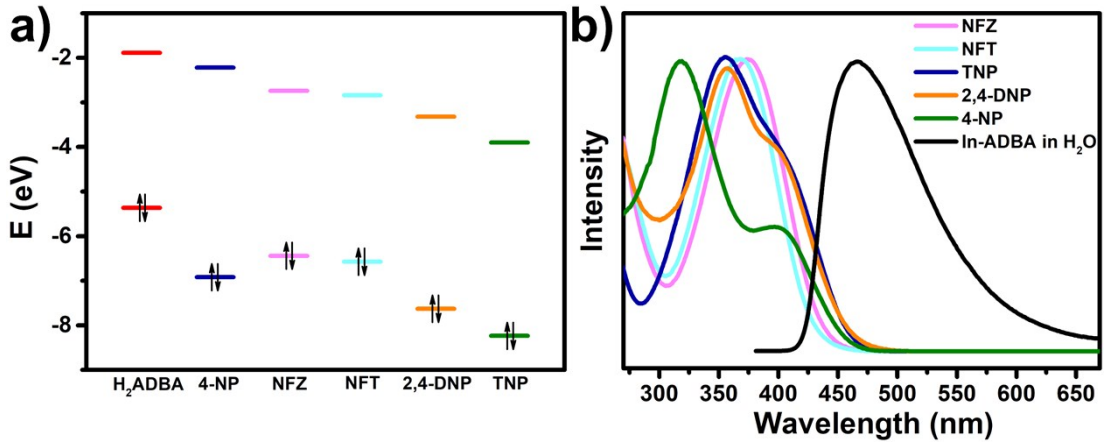

Fig. S15 a) HOMO and LUMO energies of analytes and H_2ADBA ligand, b) Spectral overlap between normalized absorption spectra of analytes and the normalized emission spectra of **In-ADBA**.

SII. Supporting Tables

Table S1. Crystal data and structure refinement for **Eu-ADBA** and **In-ADBA**.

formula	$C_{217}H_{237}O_{53}N_{19}Eu_6$	$C_{84}H_{66}O_{25}NIn_3$
formula Weight	4871.51	1833.84
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system, space group	Cubic, $Fm\bar{3}m$	Hexagonal, $P6_3/mcm$
a (Å)	33.816(4)	15.306(2)
b (Å)	33.816(4)	15.306(2)
c (Å)	33.816(4)	28.885(6)
V (Å^3)	38670(8)	5860.1(17)
Z, D_c (Mg/M^3)	220, 3.674	2, 1.039
F (000)	37400	1848
θ range (deg)	1.04~25.06	3.01~25.74
reflns collected/unique	63145/1759	30185/2043
R_{int}	0.0508	0.0420
data/restraints/params	1759/46/53	2043/61/100
GOF on F^2	1.096	1.150
R_1, wR_2 (I>2 σ (I))	R_1=0.0541, wR_2=0.1576	R_1=0.0953, wR_2=0.2334
R_1, wR_2 (all data)	R_1=0.0591, wR_2=0.1623	R_1=0.0987, wR_2=0.2350

Table S2. Photocatalytic degradation of RhB, MB and TC in water.

Catalyte	Eg (eV)	Irradiation	C_0 (mg/L)	$C_{Catalyst}$ (mg/L)	$C_{H_2O_2}$ (M)	T (min)	Efficiency (%)	k (min^{-1})	Ref.
RhB									
NNU-15(Ce)	2.11	Vis	10	600	0.6	12	99	0.2397	1
MIL-53	2.88	Vis	10	400	0.04	50	98	0.0794	2
$[Co_3(BPT)_2(DMF)(bpp)]\cdot DMF$	2.1	Vis	23.9	1000	5 drops	120	90	0.0192	3
NNU-36	2.28	Vis	10	375	1	70	96.2	0.0468	4
ST-MOF235	1.98	Vis	19.2	200	0.02	40	100	0.0039	5
NTU-9	1.72	Vis	47.9	500	5 drops	80	100	-	6
$[(Co(L)_2(H_2O)_6\cdot H_2O]_n$	1.86	Vis	9.6	3333	0.083	110	83	-	7
$[UO_2Cd(bipy)(mal)_2]\cdot H_2O$	-	UV	20	1000	-	270	94.6	-	8
$Ni(1,4\text{-}bib)_{1.5}(TPA\text{-}Cl_2)\cdot H_2O$	3.08	Vis	10	400	-	120	85.7	-	9
g-C_3N_4/MIL-125(Ti)	3.24	Vis	50	400	-	60	95.2	0.0624	10
Eu-ADBA	2.35	Vis	48	200	0.03	36	98	0.1079	This work
MB									
$\{[(CH_3)_2NH_2]_3(In_3L_4)\}\cdot(solvent)_x$	2.89	Vis	18.02	125	-	100	99	0.0438	11
NNU-36	2.28	Vis	10	375	1	80	94.2	0.0315	4
MIL-88A	2.05	Vis	37.4	400	0.004	50	100	0.01	12
$[Cu_2(mpTZ)_2Br_2]\cdot H_2O$	3.1	Vis	10	300	0.02	150	99	-	13
$[(Co(L)_2(H_2O)_6\cdot H_2O]_n$	1.86	Vis	7.4	3333	0.083	120	99	-	7
$\{[Ni^{II}(SalImCy)]_2(Cu^{I}CN)_9\}_n$	1.6	Vis	12	750	0.0625	22	99	-	14
NTU-9	1.72	Vis	31.9	500	5 drops	20	100	-	6
Fe_3O_4@MIL-100(Fe)	-	UV-Vis	40	100	0.01	200	99	0.1042	15
TiO_2NS@MIL-100(Fe)	2.87	Vis	50	400	0.02	60	98	0.045	16
ZIF-8/rGO	-	UV	10	500	-	120	51.8	0.00432	17
Eu-ADBA	2.35	Vis	32	200	0.03	30	99	0.1318	This work
TC									
$C_{52}H_{34}N_8O_{34}U_4$	2.25	Vis	40	1000	-	300	75.8	0.00485	18
$C_{29}H_{22}N_2O_{12}U_2$	2.64	Vis	40	1000	-	180	88.82	-	19
C_3N_4–ZIF-8	2.86	Vis	88.8	100	-	60	96	-	20
In_2S_3@MIL-125(Ti)	2.28	Vis	46	300	-	60	63.3	-	21
Eu-ADBA	2.35	Vis	48	200	0.03	34	98	0.1123	This work

"-" : The article does not list the data.

Table S3. Luminescent detection of nitroaromatics and antibiotics by MOFs.

MOFs	Solvent	Efficiency (%)	K_{SV} (M^{-1})	Ref.
TNP				
BUT-13	H_2O	96	5.1×10^5	22
BUT-12	H_2O	98	3.1×10^5	22
$\{[Cd_{1.5}(TPO)(bipy)_{1.5}]\cdot3H_2O\}_{2n}$	H_2O	92	1.4×10^5	23
$\{[Cd_4(L)_2(L2)_3(H_2O)_2](8DMF)(8H_2O)\}_n$	C_2H_5OH	94.28	3.89×10^4	24
$[Cd(NDC)_{0.5}(PCA)]\cdot G_x$	CH_3CN	78	3.5×10^4	25
$\{Zn_5Na_2(BPTC)_4\}n$	H_2O	96.7	3.2×10^4	26
$\{[Zn_2(L)_2(azp)]\cdot(DMF)_2\cdot(H_2O)\}_n$	H_2O	89.8	3.11×10^4	27
bio-MOF-1	H_2O	93	4.6×10^4	28
UiO-67@N	H_2O	73	2.9×10^4	29
UiO-68-mtpdc/etpdc	CH_3OH	92	2.8×10^4	30
$[Cu(L)(I)]_{2n}\cdot2nDMF\cdot nMeCN$	CH_3CN	65	2.9×10^4	31
$[Tb_2(H_2L)_3(H_2O)_2]\cdot21H_2O$	H_2O	89.4	1.5×10^4	32
In-ADBA	H_2O	92	1.282×10^5	This work
2,4-DNP				
UiO-68-mtpdc/etpdc	CH_3OH	76	2.3×10^4	30
In-ADBA	H_2O	91	8.994×10^4	This work
4-NP				
UPC-21	DMSO	98	3.097×10^6	33
BUT-13	H_2O	95	4.7×10^4	22
BUT-12	H_2O	97	4.2×10^4	22
$[Zn_2(TPOM)(NH_2\text{-}BDC)_2]\cdot4H_2O$	DMF	90	2.17×10^4	34
UPC-17	THF	75	1.26×10^4	24
$[Zn(L)(H_2O)]\cdot H_2O$	H_2O	-	1.25×10^4	35
UiO-68-mtpdc/etpdc	CH_3OH	42	7.2×10^3	30
In-ADBA	H_2O	90	5.122×10^4	This work
NFZ				
CTGU-8	H_2O	95	1.83×10^6	36
BUT-13	H_2O	95	7.5×10^4	22
BUT-12	H_2O	92	1.1×10^5	22
$[Cd_2Na(L)(BDC)_{2.5}]\cdot9H_2O$	DMF	93	5.06×10^4	37
$[Cd_2(L)(2,6\text{-}NDC)_2]\cdot DMF\cdot5H_2O$	DMF	99	1.04×10^5	37
$[Cd_2(L)(BPDC)_2]\cdot DMF\cdot9H_2O$	DMF	98	1.33×10^5	37
In-ADBA	H_2O	89	7.605×10^4	This work

NFT				
CTGU-8	H_2O	95	9.25×10^5	36
BUT-13	H_2O	94	6.0×10^4	22
BUT-12	H_2O	91	3.8×10^4	22
$[Cd_2Na(L)(BDC)_{2.5}]\cdot9H_2O$	DMF	83	3.57×10^4	37
$[Cd_2(L)(2,6\text{-}NDC)_2]\cdot DMF\cdot5H_2O$	DMF	96	7.19×10^4	37
$[Cd_2(L)(BPDC)_2]\cdot DMF\cdot9H_2O$	DMF	96	6.96×10^4	37
In-ADBA	H_2O	87	5.142×10^4	This work

"-" : The article do not list the data.

References

1. Q. Xia, X. Yu, H. Zhao, S. Wang, H. Wang, Z. Guo and H. Xing, *Cryst. Growth Des.*, 2017, **17**, 4189-4195.
2. L. Ai, C. Zhang, L. Li and J. Jiang, *Appl. Catal., B*, 2014, **148**, 191-200.
3. J. Zhao, W.-W. Dong, Y.-P. Wu, Y.-N. Wang, C. Wang, D.-S. Li and Q.-C. Zhang, *J. Mater. Chem. A*, 2015, **3**, 6962-6969.
4. H. Zhao, Q. Xia, H. Xing, D. Chen and H. Wang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 4449-4456.
5. Y. Li, G. Hou, J. Yang, J. Xie, X. Yuan, H. Yang and M. Wang, *RSC Adv.*, 2016, **6**, 16395-16403.
6. J. Gao, J. Miao, P.-Z. Li, W. Y. Teng, L. Yang, Y. Zhao, B. Liu and Q. Zhang, *Chem. Commun.*, 2014, **50**, 3786-3788.
7. Z. Shao, C. Huang, X. Han, H. Wang, A. Li, Y. Han, K. Li, H. Hou and Y. Fan, *Dalton Trans.*, 2015, **44**, 12832-12838.
8. Y.-N. Ren, W. Xu, L.-X. Zhou and Y.-Q. Zheng, *J. Solid State Chem.*, 2017, **251**, 105-112.
9. J.-W. Cui, S.-X. Hou, Y.-H. Li and G.-H. Cui, *Dalton Trans.*, 2017, **46**, 16911-16924.
10. H. Wang, X. Yuan, Y. Wu, G. Zeng, X. Chen, L. Leng and H. Li, *Appl. Catal., B*, 2015, **174**, 445-454.
11. Q. Li, D.-X. Xue, Y.-F. Zhang, Z.-H. Zhang, Z. Gao and J. Bai, *J. Mater. Chem. A*, 2017, **5**, 14182-14189.
12. W.-T. Xu, L. Ma, F. Ke, F.-M. Peng, G.-S. Xu, Y.-H. Shen, J.-F. Zhu, L.-G. Qiu and Y.-P. Yuan, *Dalton Trans.*, 2014, **43**, 3792-3798.
13. J.-Y. Zhang, Y.-Y. Xing, Q.-W. Wang, N. Zhang, W. Deng and E.-Q. Gao, *J. Solid State Chem.*, 2015, **232**, 19-25.
14. Y.-L. Hou, S.-X. Li, R. W.-Y. Sun, X.-Y. Liu, S. W. Ng and D. Li, *Dalton Trans.*, 2015, **44**, 17360-17365.
15. C.-F. Zhang, L.-G. Qiu, F. Ke, Y.-J. Zhu, Y.-P. Yuan, G.-S. Xu and X. Jiang, *J. Mater. Chem. A*, 2013, **1**, 14329-14334.
16. X. Liu, R. Dang, W. Dong, X. Huang, J. Tang, H. Gao and G. Wang, *Appl. Catal., B*, 2017, **209**, 506-513.
17. J. Mao, M. Ge, J. Huang, Y. Lai, C. Lin, K. Zhang, K. Meng and Y. Tang, *J. Mater. Chem. A*, 2017, **5**, 11873-11881.
18. Y.-N. Ren, W. Xu, L.-X. Zhou and Y.-Q. Zheng, *Polyhedron*, 2018, **139**, 63-72.
19. W. Xu, Z.-X. Si, M. Xie, L.-X. Zhou and Y.-Q. Zheng, *Cryst. Growth Des.*, 2017, **17**, 2147-

2157.
20. S. Panneri, M. Thomas, P. Ganguly, B. N. Nair, A. P. Mohamed, K. Warrier and U. Hareesh, *Catal. Sci. Technol.*, 2017, **7**, 2118-2128.
21. H. Wang, X. Yuan, Y. Wu, G. Zeng, H. Dong, X. Chen, L. Leng, Z. Wu and L. Peng, *Appl. Catal., B*, 2016, **186**, 19-29.
22. B. Wang, X.-L. Lv, D. Feng, L.-H. Xie, J. Zhang, M. Li, Y. Xie, J.-R. Li and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204-6216.
23. K. Xing, R. Fan, J. Wang, S. Zhang, K. Feng, X. Du, Y. Song, P. Wang and Y. Yang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 19881-19893.
24. T. K. Pal, N. Chatterjee and P. K. Bharadwaj, *Inorg. Chem.*, 2016, **55**, 1741-1747.
25. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2013, **52**, 2881-2885.
26. E.-L. Zhou, P. Huang, C. Qin, K.-Z. Shao and Z.-M. Su, *J. Mater. Chem. A*, 2015, **3**, 7224-7228.
27. S. Senthilkumar, R. Goswami, N. L. Obasi and S. Neogi, *ACS Sustainable Chem. Eng.*, 2017, **5**, 11307-11315.
28. B. Joarder, A. V. Desai, P. Samanta, S. Mukherjee and S. K. Ghosh, *Chemistry-A European Journal*, 2015, **21**, 965-969.
29. S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Commun.*, 2014, **50**, 8915-8918.
30. Q.-Y. Li, Z. Ma, W.-Q. Zhang, J.-L. Xu, W. Wei, H. Lu, X. Zhao and X.-J. Wang, *Chem. Commun.*, 2016, **52**, 11284-11287.
31. S. Khatua, S. Goswami, S. Biswas, K. Tomar, H. S. Jena and S. Konar, *Chem. Mater.*, 2015, **27**, 5349-5360.
32. R. Fu, S. Hu and X. Wu, *J. Mater. Chem. A*, 2017, **5**, 1952-1956.
33. M. Zhang, L. Zhang, Z. Xiao, Q. Zhang, R. Wang, F. Dai and D. Sun, *Sci. Rep.*, 2016, **6**, 20672.
34. R. Lv, J. Wang, Y. Zhang, H. Li, L. Yang, S. Liao, W. Gu and X. Liu, *J. Mater. Chem. A*, 2016, **4**, 15494-15500.
35. X.-Y. Guo, F. Zhao, J.-J. Liu, Z.-L. Liu and Y.-Q. Wang, *J. Mater. Chem. A*, 2017, **5**, 20035-20043.
36. Z.-H. Zhou, W.-W. Dong, Y.-P. Wu, J. Zhao, D.-S. Li, T. Wu and X.-h. Bu, *Inorg. Chem.*, 2018, **57**, 3833-3839.
37. D. Zhao, X.-H. Liu, Y. Zhao, P. Wang, Y. Liu, M. Azam, S. I. Al-Resayes, Y. Lu and W.-Y. Sun, *J. Mater. Chem. A*, 2017, **5**, 15797-15807.