

Supporting Information

Acetylacetonate Functionalized Periodic Mesoporous Organosilicas: from Sensing to Catalysis

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Table S 1 The comparisons of the sensing performance for different nanoparticle fluorometric sensors in aqueous solution.

Fluorescence probe	Materials	Analytes detected	Linear range	K_{sv} (M^{-1})	LOD	Ref
NS-CQDs	carbon quantum dots (CQDs)	Cu^{2+}	0 – 1 μM	-	1.65 μM	1
SiO_2/CdS NCs	nanocrystals	Cu^{2+}	0 – 3 μM	-	$3.5 \times 10^{-2} \mu M$	2
ZCM microsphere	QD composite	Cu^{2+} , Cr^{2+} , Fe^{3+}	0 – 1 μM	3.85×10^5	$1.6 \times 10^{-5} \mu M$	3
CE/11-MUA-AuNCs	gold nanoclusters	Cu^{2+} , Cd^{2+} , Zn^{2+}	0.05–10 μM	-	0.026 μM	4
AlEgens fabricated on nanoscale ZIF-8	aggregation-induced emission luminogens with MOFs	Cu^{2+}	0 – 0.1 μM	-	$5.5 \times 10^{-4} \mu M$	5
$[Ce(1,5-NDS)_{1.5}(H_2O)_5]_n$	MOFs	Cu^{2+}	5 - 100 μM	7668	3 μM	6
AuNCs/PQD@ SiO_2	gold nanocomposites	Cu^{2+}	0 - 160 μM	4400	3 μM	7
QG-scaffolded COFs	COFs	Cu^{2+}	0.0032 - 32 μM	-	$5 \times 10^{-4} \mu M$	8
$[Eu(bpdc)_{1.5}(H_2O)_2]_n$	Eu-MOFs	Fe^{3+} , Cu^{2+} , PO_4^{3-}	0 – 400 μM	3240	33 μM	9
$\{[Eu(L)(DMF)(H_2O)] \cdot 0.5DMF\}_n$	Eu-MOFs	Cu^{2+}	0.01 - 1000 μM	4.3×10^4	$1.02 \times 10^3 \mu M$	10
$[Eu(L)(DEF)(H_2O)]_n$	Eu-MOFs	Cu^{2+}	0.01 - 1000 μM	5.7×10^4	$5 \times 10^4 \mu M$	11
Eu-MOFs (4, 40-AZ, DMF and H_3BTC)	Eu-MOFs	Cu^{2+}	2 - 1000 μM	2.9×10^4	1.395 μM	11
$\{[Tb(HL)] \cdot 3DMF \cdot 3H_2O\}_n$ (LZG-Tb)	Tb-MOFs	Cu^{2+}	0 - 0.25 μM	8.2×10^6	$1.65 \times 10^3 \mu M$	12
$\{[Eu(HL)] \cdot 3DMF \cdot 3H_2O\}_n$ (LZG-Eu)	Eu-MOFs	Cu^{2+}	0 - 0.25 μM	4.9×10^6	$1.35 \times 10^3 \mu M$	12
TH-PMO-100	PMOs	Cu^{2+}	0.1 - 1 μM	1.6×10^4	40 μM	13
RSPMOs	PMOs	Cu^{2+}	0.1 - 1 μM	-	0.1 μM	14
SCN-PMO	PMOs	Cu^{2+}	8.75 - 20 μM	-	0.67 μM	15
Ag-PMO-YS	nanocomposites	Cu^{2+}	0.1 - 9 μM	-	0.02 μM	16
$Eu(NTA)_3L-COOH-PMO$	Eu-PMOs	Cu^{2+}	0 - 20 μM	2.5×10^6	0.046 μM	17
ePMO@Eu_PA	Eu-PMOs	Cu^{2+}	0 - 400 μM	2100	35.2 μM	18
acac(20)-PMO@Eu_tta	Eu-PMOs	Cu^{2+}	0 - 2.5 μM	1.8×10^5	0.108 μM	This work

Table S 2 Comparison of the acac-PMO catalyst with other VO(acac)₂ based catalysts.

Entry	Catalyst	Reaction conditions	Yield (%)	TON ^a	Ref
1	VO(acac) ₂	catalyst (10 mol %), CH_2Cl_2 , reflux, 8 h	92	9.2	19
2	VO-TAPT-2,3-DHTA COF	catalyst (35 mg, 0.97 mmol/g V), DCM, 40 °C, 12 h	98	29	20
3	VO-PyTTA-2,3-DHTA COF	catalyst (35 mg, 0.77 mmol/g V), DCM, 40 °C, 12 h	96	36	20
3	V@acac-CTF	catalyst (40 mg, 0.306 mmol/g V), DCM, 40 °C, 8 h	95	213	21
4	acac(100)-PMO@VO_acac	catalyst (15 mg, 0.59 mmol/g V), DCM, 40 °C, 12 h	98	111	This work

^a TON = turnover number

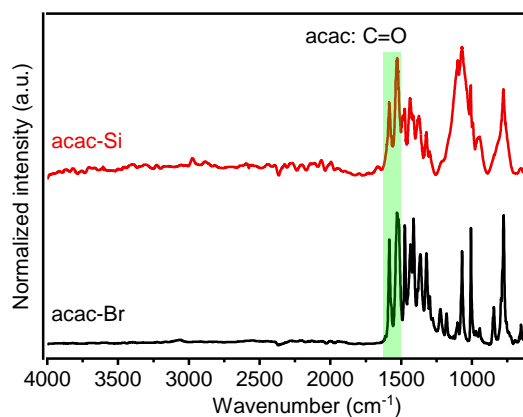


Figure S1. FT-IR spectra of acac-Br and acac-Si.

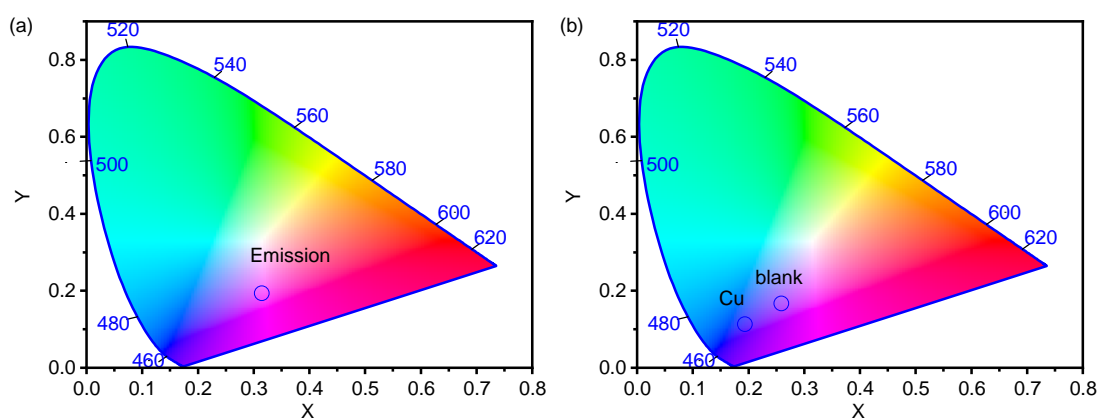


Figure S2. CIE chromaticity diagram of (a) solid acac(20)-PMO@Eu_tta; (b) colloidal suspensions of acac(20)-PMO@Eu_tta with and without Cu²⁺.

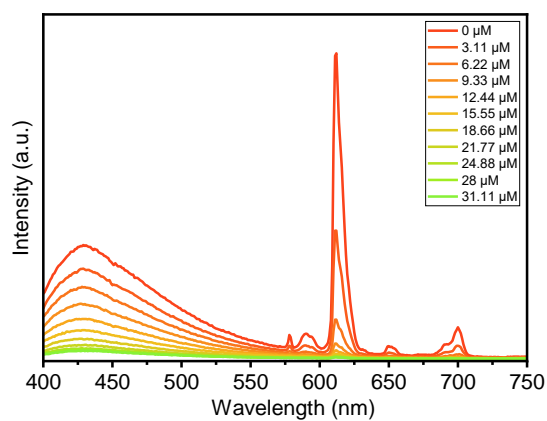


Figure S3. Luminescence spectra of acac(20)-PMO@Eu_tta under different concentrations of Cu²⁺ aqueous solutions.

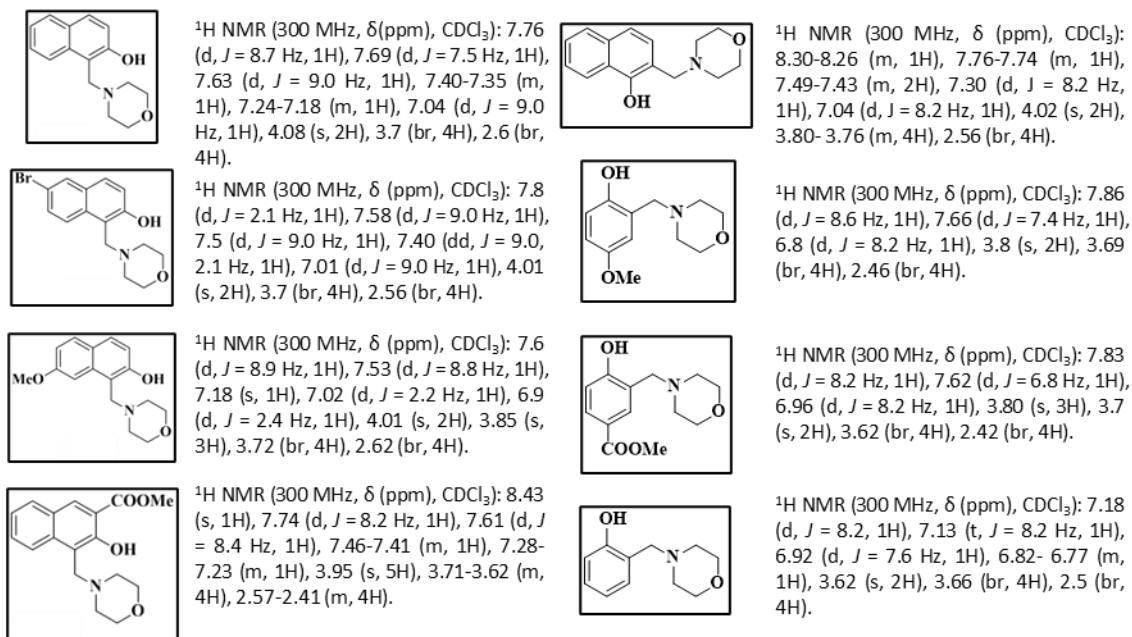


Figure S4. $^1\text{H-NMR}$ data of Mannich-reaction product in CDCl_3 .

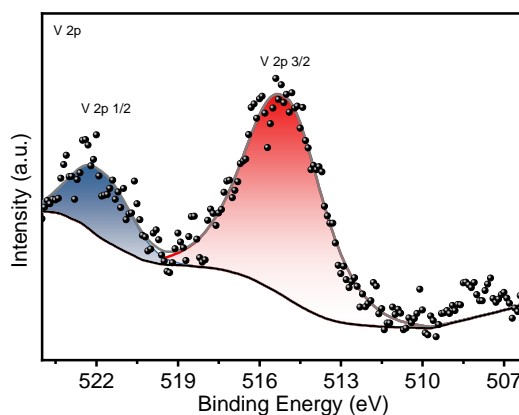


Figure S5. Deconvoluted XPS spectra of vanadium in the V 2p region for acac(100)-PMO@VO_acac catalyst.

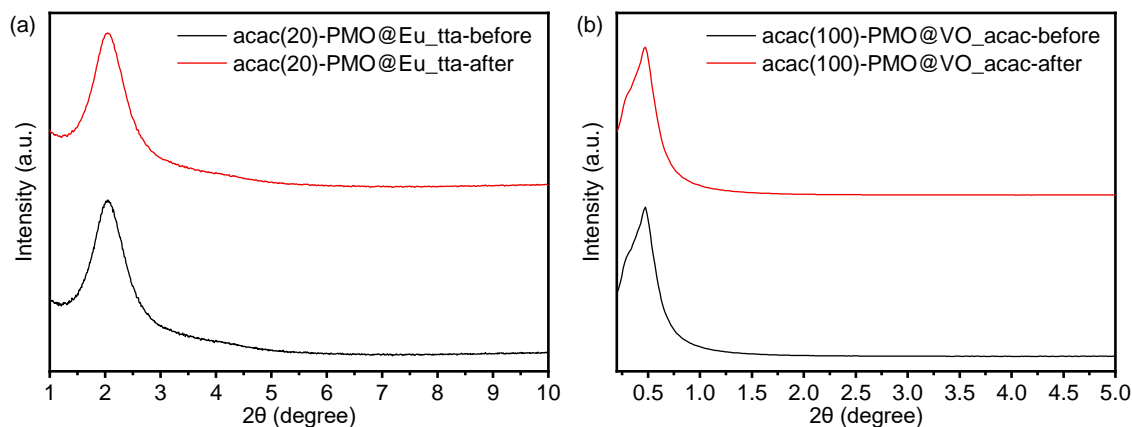
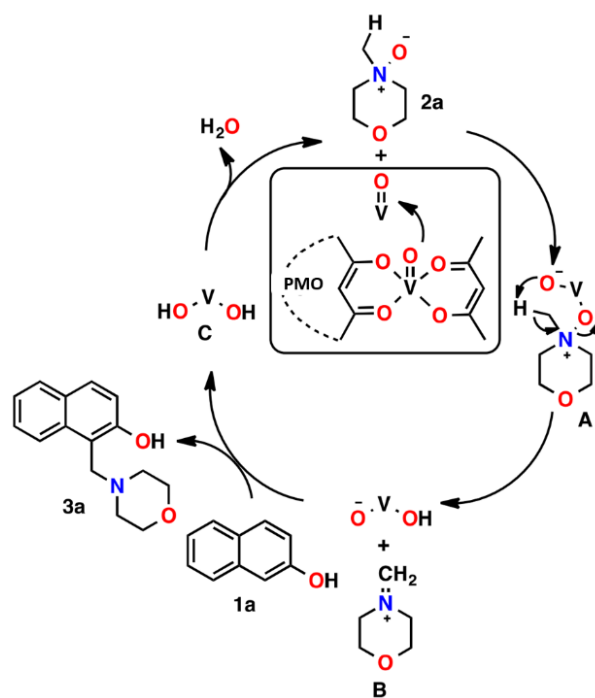


Figure S6. (a) XRD patterns of acac(20)-PMO@Eu_tta before and after immersing in water with Cu^{2+} ions and (b) XRD patterns of acac(100)-PMO@VO_acac before and after catalysis.



Scheme S 1 Proposed mechanism of Mannich-type reaction catalyzed by acac(100)-PMO@VO₂.

References

1. N. Chaudhary, P. K. Gupta, S. Eremin and P. R. Solanki, *J. Environ. Chem. Eng.*, 2020, 8, 103720.
2. T. Xie, X. Zhong, Z. Liu and C. Xie, *Mikrochim. Acta*, 2020, 187, 323.
3. M. M. R. Khan, T. Mitra and D. Sahoo, *RSC Adv*, 2020, 10, 9512-9524.
4. M. L. Desai, H. Basu, S. Saha, R. K. Singhal and S. K. Kailasa, *J. Mol. Liq.*, 2020, 304, 112697.
5. S. Xie, Q. Liu, F. Zhu, M. Chen, L. Wang, Y. Xiong, Y. Zhu, Y. Zheng and X. Chen, *J Mater Chem C*, 2020, 8, 10408-10415.
6. S. Geranmayeh, M. Mohammadnejad and S. Mohammadi, *Ultrason Sonochem*, 2018, 40, 453-459.
7. W. Xue, J. Zhong, H. Wu, J. Zhang and Y. Chi, *Analyst*, 2021, 146, 7545-7553.
8. Y. Y. Cai, Y. Jiang, L. P. Feng, Y. Hua, H. Liu, C. Fan, M. Y. Yin, S. Li, X. X. Lv and H. Wang, *Anal. Chim. Acta*, 2019, 1057, 88-97.
9. Z. D. Li, Z. Y. Zhan, Y. J. Jia, Z. Li and M. Hu, *J Ind Eng Chem*, 2021, 97, 180-187.
10. R. R. Ma, Z. W. Chen, S. N. Wang, Q. X. Yao, Y. W. Li, J. Lu, D. C. Li and J. M. Dou, *J Solid State Chem*, 2017, 252, 142-151.
11. J. C. Zhou, Y. H. Chen, S. Xian, Y. C. Liang, G. J. Huang, L. Wang and X. Z. Yang, *J Solid State Chem*, 2021, 304, 122542.
12. Z. G. Lin, F. Q. Song, H. Wang, X. Q. Song, X. X. Yu and W. S. Liu, *Dalton Trans.*, 2021, 50, 1874-1886.
13. M. Gao, S. Han, Y. Hu and L. Zhang, *J. Phys. Chem. C*, 2016, 120, 9299-9307.
14. X. Y. Qiu, S. H. Han and M. Gao, *J. Mater. Chem. A*, 2013, 1, 1319-1325.
15. M. Gao, C. Xing, X. Jiang, L. Xu, P. Li and C. D. Hsiao, *J. Lumin.*, 2021, 36, 951-957.
16. L. Yang, S. Shen, J. Zhu, Y. Zhang, Y. Lin, J. Wang, F. Tao, L. Wang and J. Zhang, *ACS Appl. Nano Mater.*, 2023, 6, 1910-1918.
17. H. Li, Y. J. Li, Z. Zhang, X. L. Pang and X. D. Yu, *Mater Design*, 2019, 172, 107712.
18. W. Liu, A. M. Kaczmarek, H. Rijckaert, P. Van Der Voort and R. Van Deun, *Dalton Trans*, 2021, 50, 11061-11070.

19. D. R. Hwang and B. J. Uang, *Org. Lett.*, 2002, 4, 463-466.
20. H. Vardhan, L. X. Hou, E. Yee, A. Nafady, M. A. Al-Abdrabalnabi, A. M. Al-Enizi, Y. X. Pan, Z. Y. Yang and S. Q. Ma, *Acs Sustain Chem Eng*, 2019, 7, 4878-4888.
21. H. S. Jena, C. Krishnaraj, G. B. Wang, K. Leus, J. Schmidt, N. Chaoui and P. Van der Voort, *Chem. Mater.*, 2018, 30, 4102-4111.