Supplementary Information

A dual-emission Nano-Rod MOF equipped with carbon dots for visual detecting doxycycline and sensitive sensing MnO_4^-

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Supporting Figures

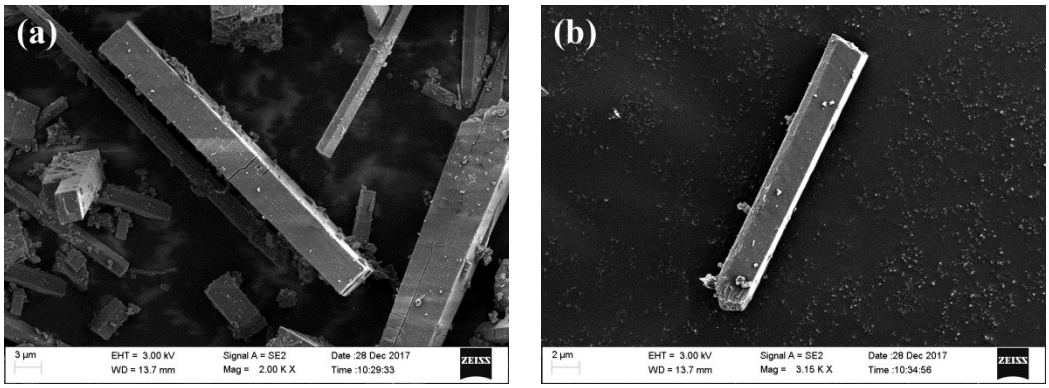

Fig. S1 The SEM pictures of (a) MOF(Eu) and (b) CDs@MOF(Eu).

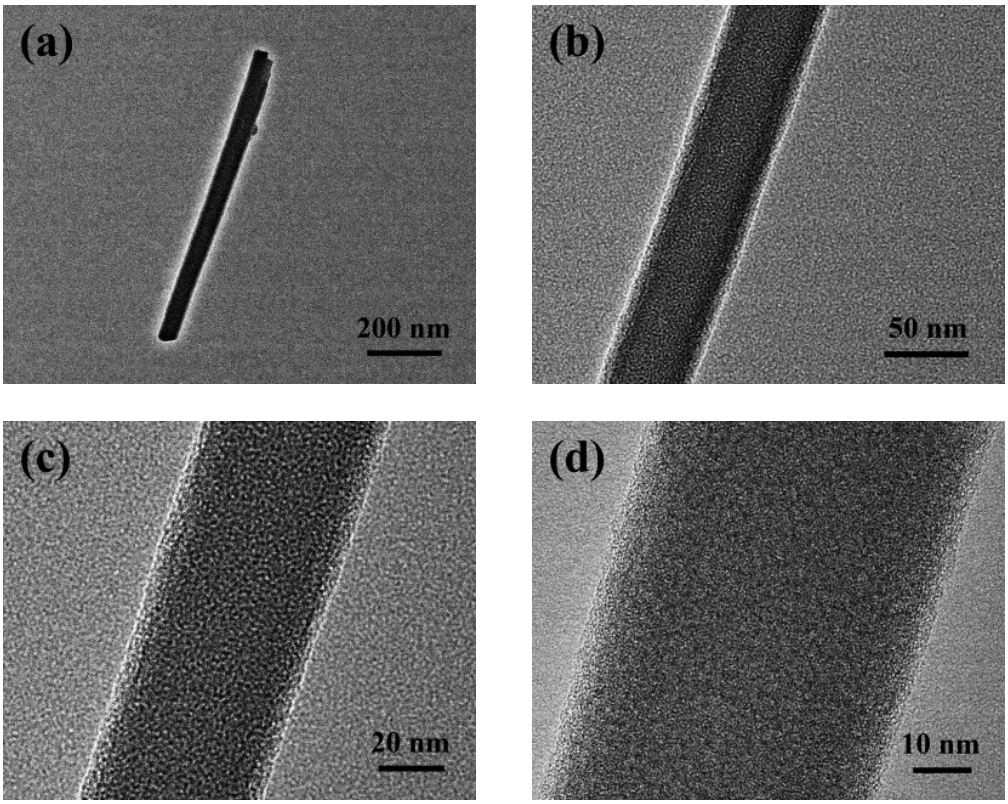

Fig. S2 The microstructure TEM pictures of CDs@MOF(Eu) under different magnification.

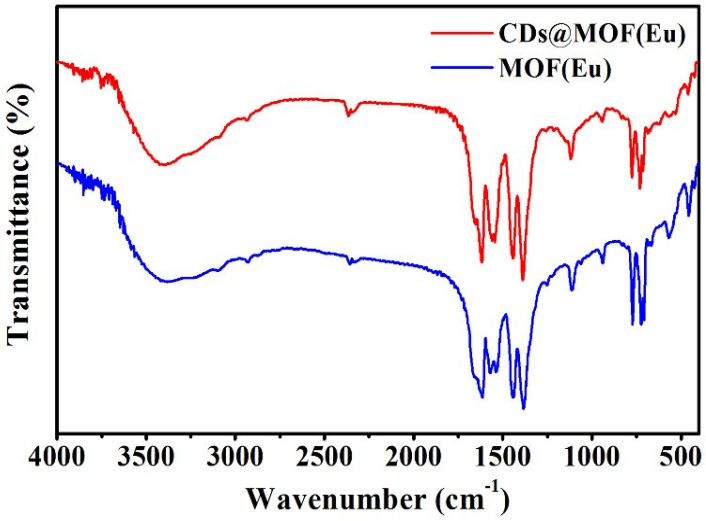

Fig. S3 FT-IR spectra of MOF(Eu) and CDs@MOF(Eu).

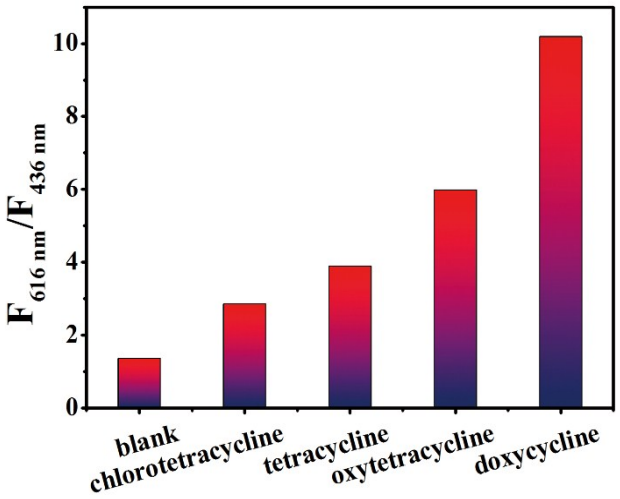

Fig. S4 The specificity comparison of four tetracycline antibiotics.

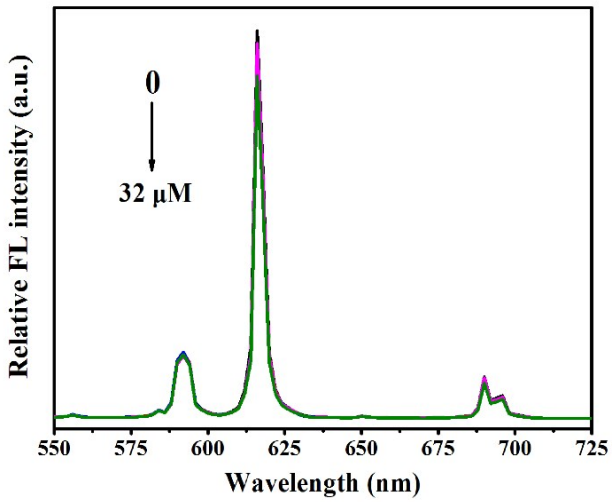

Fig. S5 Emission spectra of MOF(Eu) adding MnO_4^- (0-32 μM).

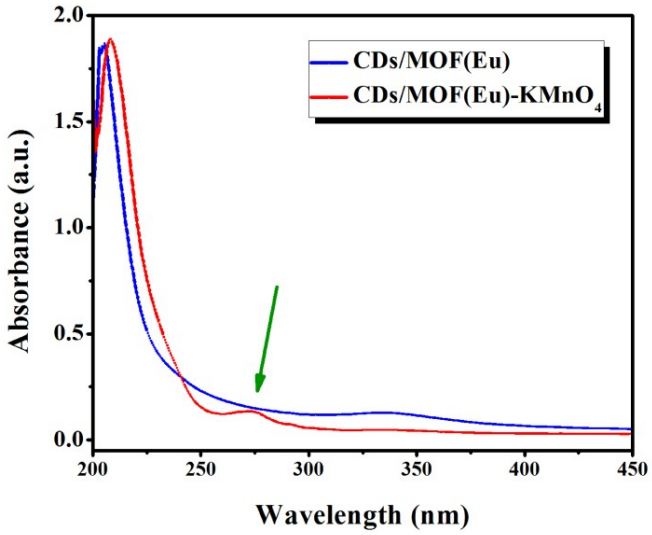

Fig. S6 The absorption spectrum of CDs@MOF(Eu) before and after adding $KMnO_4$.

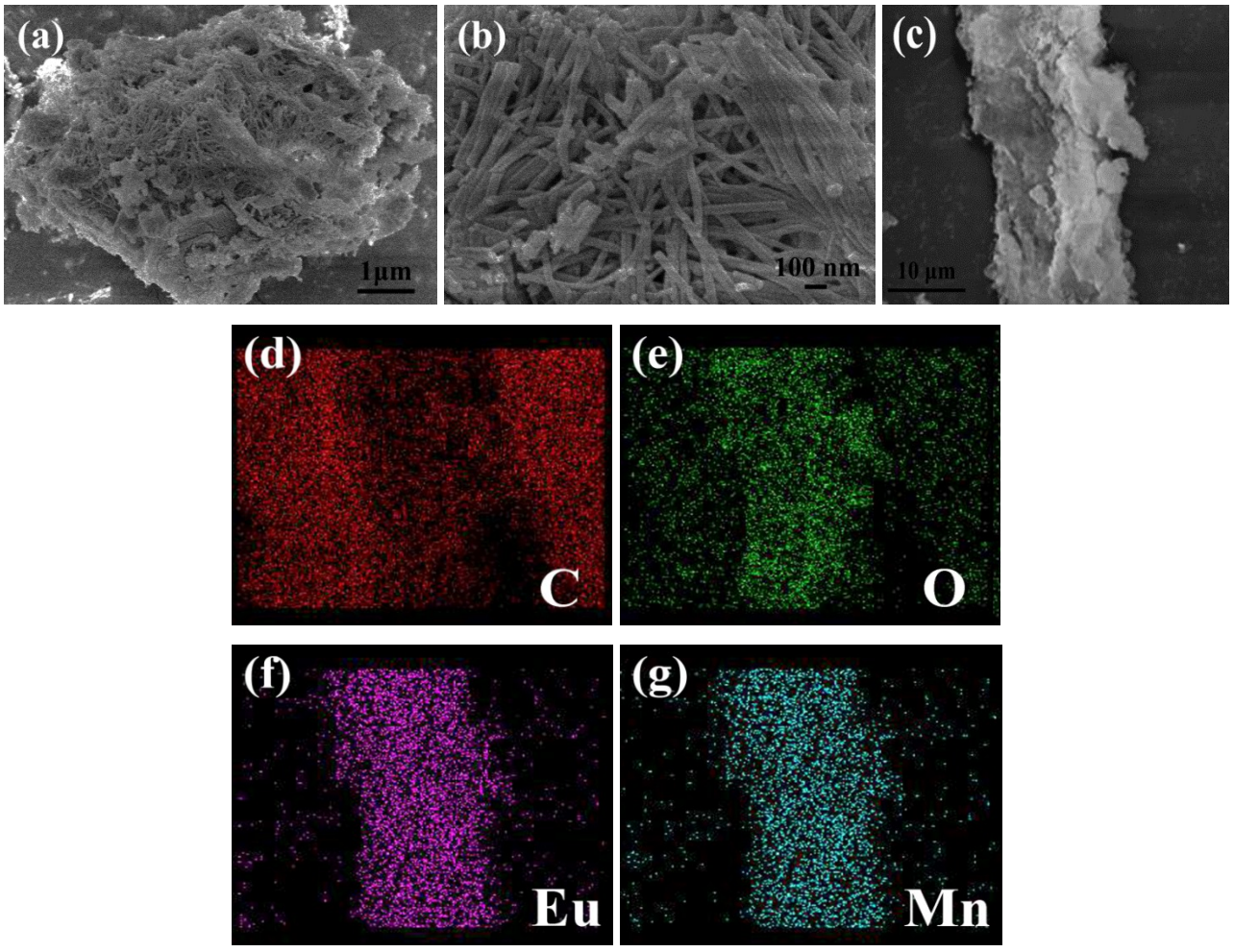

Fig. S7 SEM images of (a)-(c) CDs@MOF(Eu)-$KMnO_4$ hybrid system and the corresponding element mapping images of (d) C; (e) O; (f) Eu; (g) Mn recorded from (c).

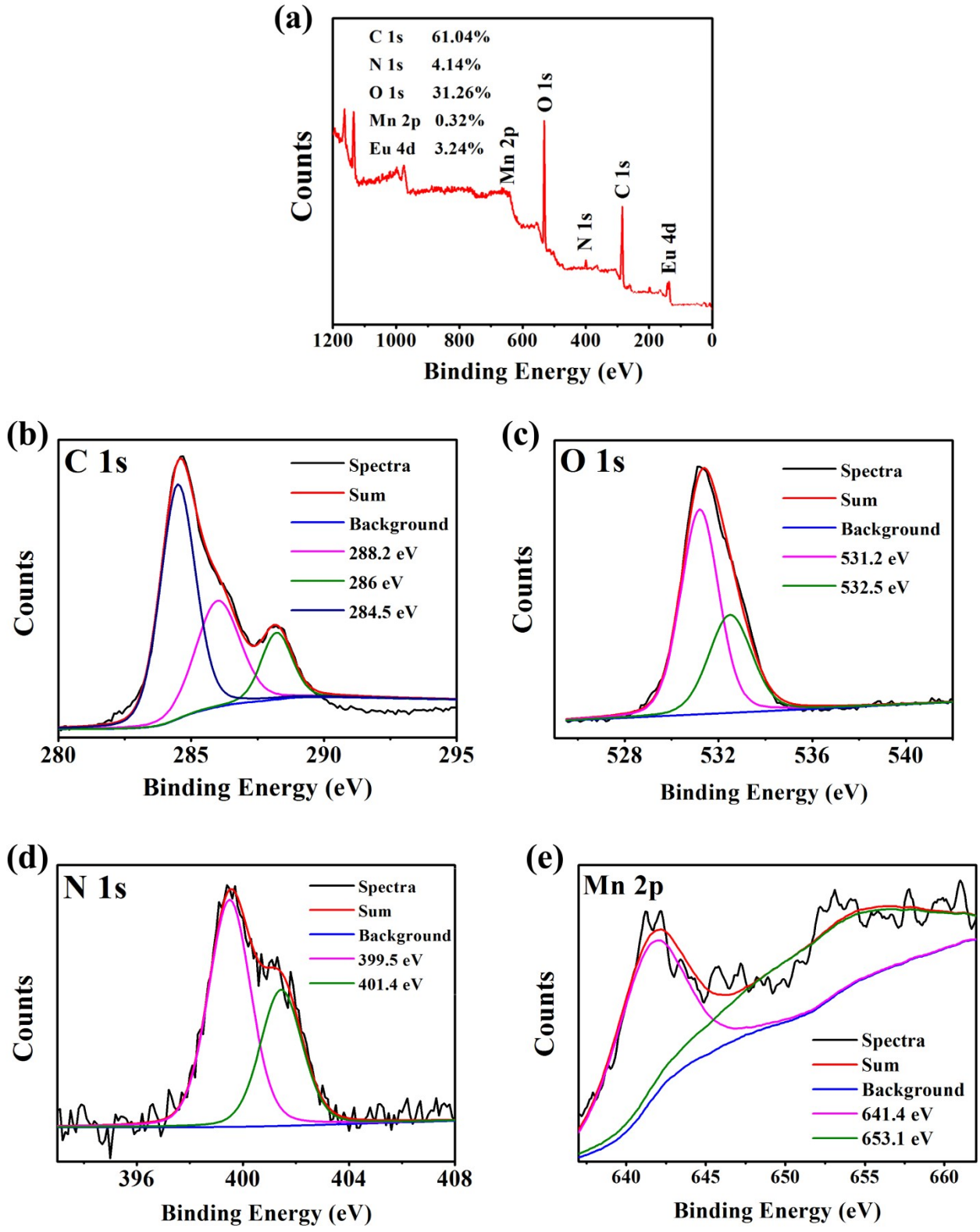

Fig. S8 (a) XPS broad scans; (b) C1s XPS spectrum; (c) O1s XPS spectrum; (d) N1s XPS spectrum and (e) Mn2p XPS spectrum of CDs@MOF(Eu)-$KMnO_4$ hybrid system.

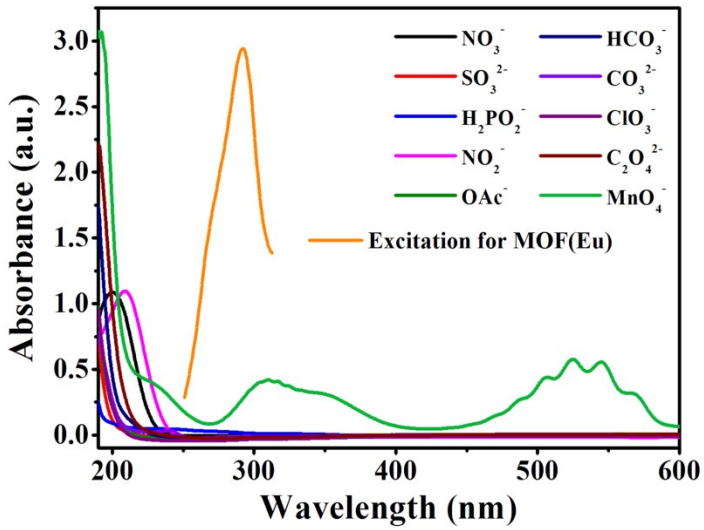

Fig. S9 The absorption spectrum of different anions and the excitation for MOF(Eu).

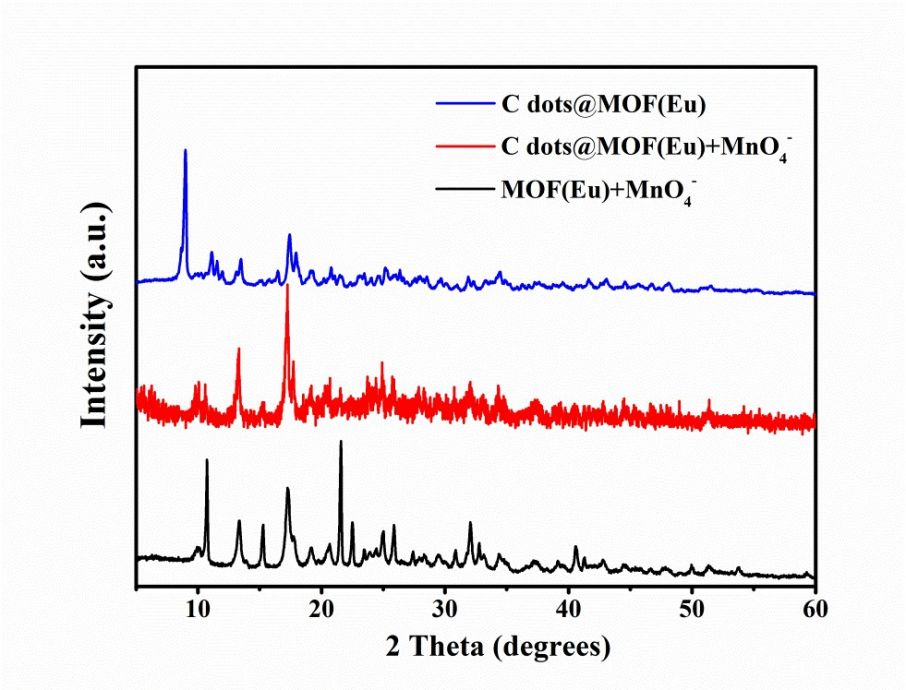

Fig. S10 XRD patterns of CDs@MOF(Eu), CDs@MOF(Eu)-$KMnO_4$ hybrid system and MOF(Eu)-$KMnO_4$ hybrid system.

Supporting Tables

Table S1 Comparison of analytical performance of doxycycline with traditional methods.

Method	Linear detection range	LOD	References
Sequential injection chromatography (SIC)	2-100 μg/mL	4.325 μM	[1]
Micellar electrokinetic capillary chromatography (MEKC)	1.04×10^{-5}-1.90×10^{-4} M	2.0 μM	[2]
High-performance liquid chromatography with UV detection	25.2 – 252 μg/mL	1.15 μg/mL	[3]
Molecularly imprinted polymers-based electrochemical method	50 – 500 μM	42.5 μM	[4]
CDs@MOF(Eu) hybrid material	0-60 μM	0.36 μM (0.1665 μg/mL)	This work

Table S2 Comparison of analytical performance of the MnO_4^- with other materials.

Method	Linear detection range	LOD	References
In-MOF-Eu	0-500 μM	1.47×10^{-4} μM	[5]
Tyloxapol	0-120 μM	0.3924 μM	[6]
534-MOF-Tb	——	0.34 mM	[7]
[Pb(BPDP)] (1) and $[Pb_3(BPDP)_{1.5}(OOCC_6H_4COOH)_3]$ (2)	10-100 μM	——	[8]
CDs@MOF(Eu) hybrid material	0-100 μM	0.68 μM	This work

References

1. D. Šatínský, L. M. L. Dos Santos, H. Skelenářová, P. Solich, M. C. B. S. M. Montenegro and A. N. Araújo, *Talanta*, 2005, **68**, 214-218.
2. R. Injac, J. Kac, S. Kreft and B. Strukelj, *Anal. Bioanal. Chem.*, 2007, **387**, 695–701.
3. S. S. Mittić, G. Ž. Miletić, D. A. Kostić, D. Č. Nasković-Đokić, B. B. Arsić and I. D. Rašić, *J.Serb.Chem.Soc.*, 2008, **73**, 665-671.
4. B. Gürler, S. F. Özkorucuklu and E. Kır, *J.Pharm.Biomed.Anal.*, 2013, **84**, 263-268.
5. J. X. Wu, B. Yan, *Journal of Colloid and Interface Science*, 2017, **504**, 197-205.
6. P. Ding, X. Xin, L. L. Zhao, Z. C. Xie, Q. H. Zhang, J. M. Jiao and G. Y. Xu, *RSC Adv.*, 2017, **7**, 3051-3058.
7. M. Chen, W. M. Xu, J. Y. Tian, H. Cui, J. X. Zhang, C. S. Liu and M. Du, *J. Mater. Chem. C*, 2017, **5**, 2015-2021.
8. B. Xing, H. Y. Li, Y. Y. Zhu, Z. Zhao, Z. G. Sun, D. Yang and J. Li, *RSC Adv.*, 2016, **6**, 110255–110265.