Supporting information

Spontaneous chiral resolution of a rare 3D self-penetration coordination polymer for sensitive aqueous-phase detection of picric acid

Bai-Qiao Song, Chao Qin*, Yu-Teng Zhang, Xue-Song Wu, Liu Yang, Kui-Zhan Shao and Zhong-Min Su*

Institute of Functional Material Chemistry; Key Laboratory of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China; E-mail: qinc703@nenu.edu.cn, zmsu@nenu.edu.cn

Table S1. Selected bond lengths (Å) and bond angles (°).

Bond lengths (Å)			
1R		**1L**	
Cd(1)-O(3)	2.225(3)	N(1)-Cd(1)	2.281(3)
Cd(1)-N(7)	2.285(3)	N(3)-Cd(1)#5	2.402(3)
Cd(1)-O(2)#1	2.350(3)	N(5)-Cd(1)	2.410(3)
Cd(1)-N(6)#2	2.396(3)	O(1)-Cd(1)	2.223(3)
Cd(1)-O(1)#1	2.503(3)	O(3)-Cd(1)	2.355(3)
Cd(1)-N(1)	2.407(3)	O(4)-Cd(1)	2.505(3)
N(6)-Cd(1)#6	2.396(3)	Cd(1)-N(3)#6	2.402(3)
Bond angles (°)			
1R		**1L**	
O(3)-Cd(1)-N(7)	118.82(11)	C(1)-N(1)-Cd(1)	126.5(2)
O(3)-Cd(1)-O(2)#1	95.36(10)	C(2)-N(1)-Cd(1)	127.9(2)
N(7)-Cd(1)-O(2)#1	101.82(10)	C(18)-N(3)-Cd(1)#5	123.2(2)
O(3)-Cd(1)-N(6)#2	80.55(10)	C(19)-N(3)-Cd(1)#5	124.8(2)
N(7)-Cd(1)-N(6)#2	157.55(10)	C(11)-N(5)-Cd(1)	133.1(2)
O(2)#1-Cd(1)-N(6)#2	86.41(10)	N(6)-N(5)-Cd(1)	118.49(19)
O(3)-Cd(1)-N(1)	100.12(10)	C(21)-O(1)-Cd(1)	112.4(2)
N(7)-Cd(1)-N(1)	87.78(9)	C(22)-O(3)-Cd(1)	93.4(2)
O(2)#1-Cd(1)-N(1)	155.01(10)	C(22)-O(4)-Cd(1)	86.8(2)
N(6)#2-Cd(1)-N(1)	77.00(9)	O(1)-Cd(1)-N(1)	118.68(11)
O(3)-Cd(1)-O(1)#1	143.12(9)	O(1)-Cd(1)-O(3)	95.32(10)
N(7)-Cd(1)-O(1)#1	89.78(9)	N(1)-Cd(1)-O(3)	101.83(10)
O(2)#1-Cd(1)-O(1)#1	53.65(9)	O(1)-Cd(1)-N(3)#6	80.50(10)
N(6)#2-Cd(1)-O(1)#1	78.26(9)	N(1)-Cd(1)-N(3)#6	157.67(10)
N(1)-Cd(1)-O(1)#1	104.03(9)	O(3)-Cd(1)-N(3)#6	86.55(10)
C(1)-N(1)-Cd(1)	133.3(2)	O(1)-Cd(1)-N(5)	100.06(11)
N(2)-N(1)-Cd(1)	118.6(2)	N(1)-Cd(1)-N(5)	87.86(10)
C(10)-N(6)-Cd(1)#6	123.3(2)	O(3)-Cd(1)-N(5)	155.08(11)
C(11)-N(6)-Cd(1)#6	125.0(2)	N(3)#6-Cd(1)-N(5)	76.89(9)
C(12)-N(7)-Cd(1)	126.1(2)	O(1)-Cd(1)-O(4)	143.02(10)
C(13)-N(7)-Cd(1)	127.8(2)	N(1)-Cd(1)-O(4)	90.06(9)
C(22)-O(1)-Cd(1)#5	86.7(2)	O(3)-Cd(1)-O(4)	53.70(10)
C(22)-O(2)-Cd(1)#5	93.7(2)	N(3)#6-Cd(1)-O(4)	78.18(9)
C(21)-O(3)-Cd(1)	112.0(3)	N(5)-Cd(1)-O(4)	104.03(10)

Symmetry transformations used to generate equivalent atoms: **1R**: #1 -y+1,x+1,z+1/4; #2 -y,x,z+1/4; #3 -y,x-1,z+1/4; #4 y+1,-x,z-1/4; #5 y-1,-x+1,z-1/4; #6 y,-x,z-1/4; **1L**: #1 -y+1,x-1,z-1/4; #2 y+1,-x+1,z+1/4; #3 y-1,-x,z+1/4; #4 -y,x+1,z-1/4; #5 -y+1,x,z-1/4; #6 y,-x+1,z+1/4;

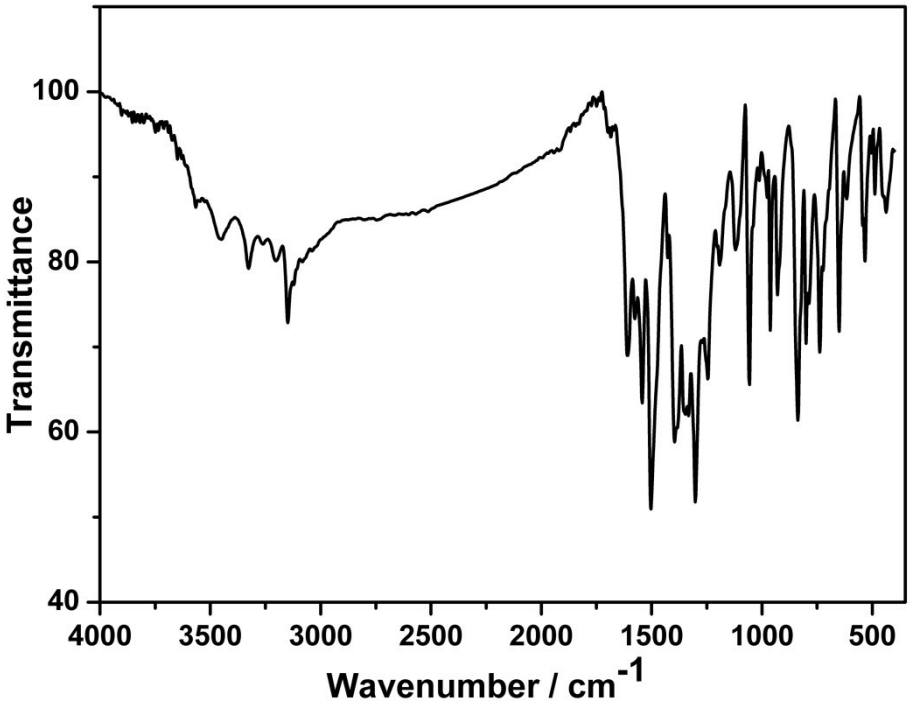

Figure S1. Infrared spectrum of fresh **1.**

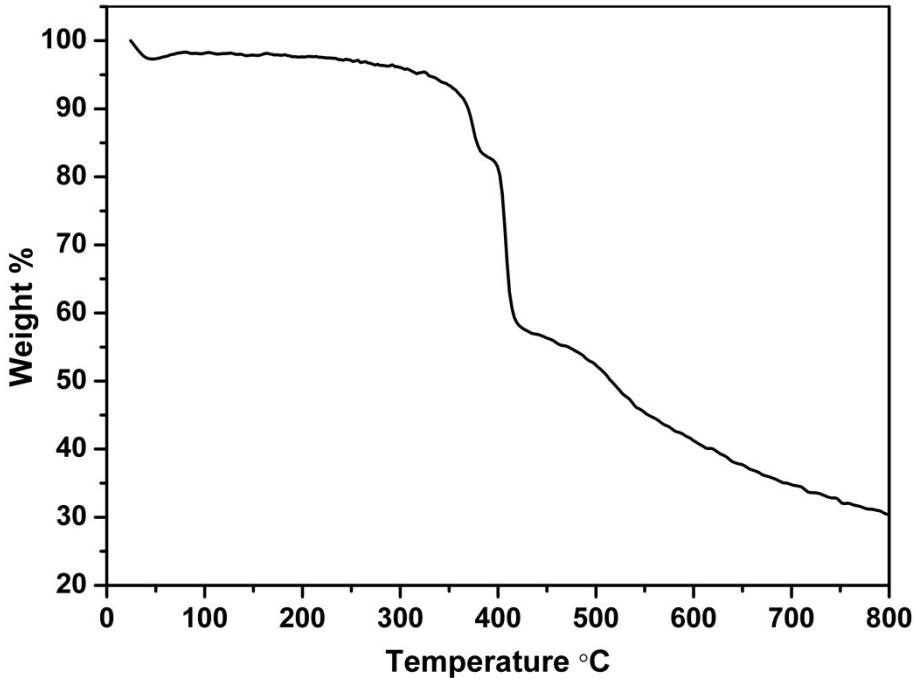

Figure S2. TGA curve of compound **1**.

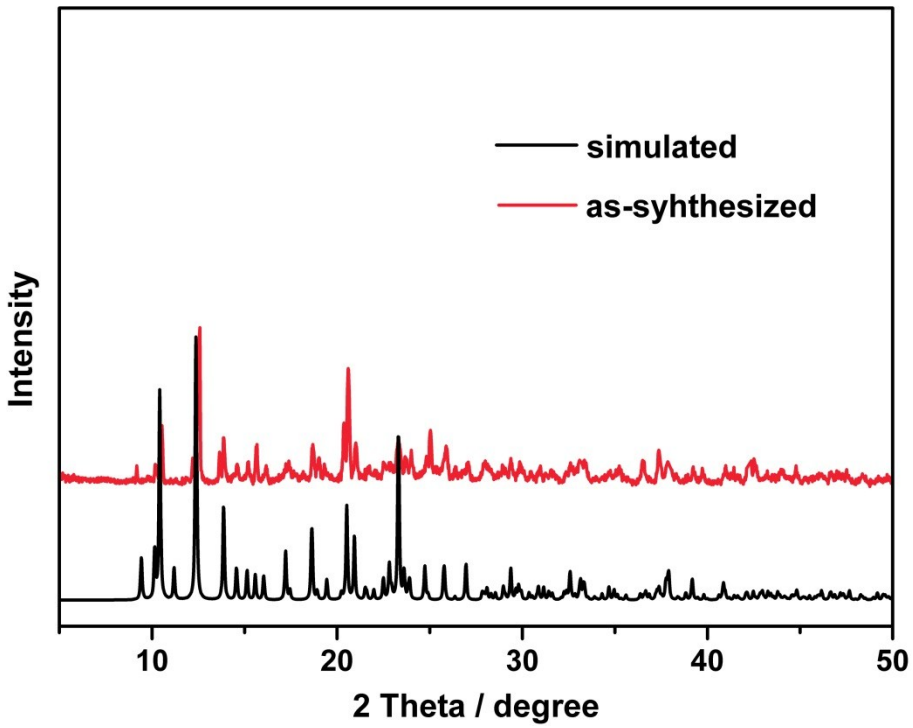

Figure S3. PXRD profiles of as-synthesized **1** and the simulated one.

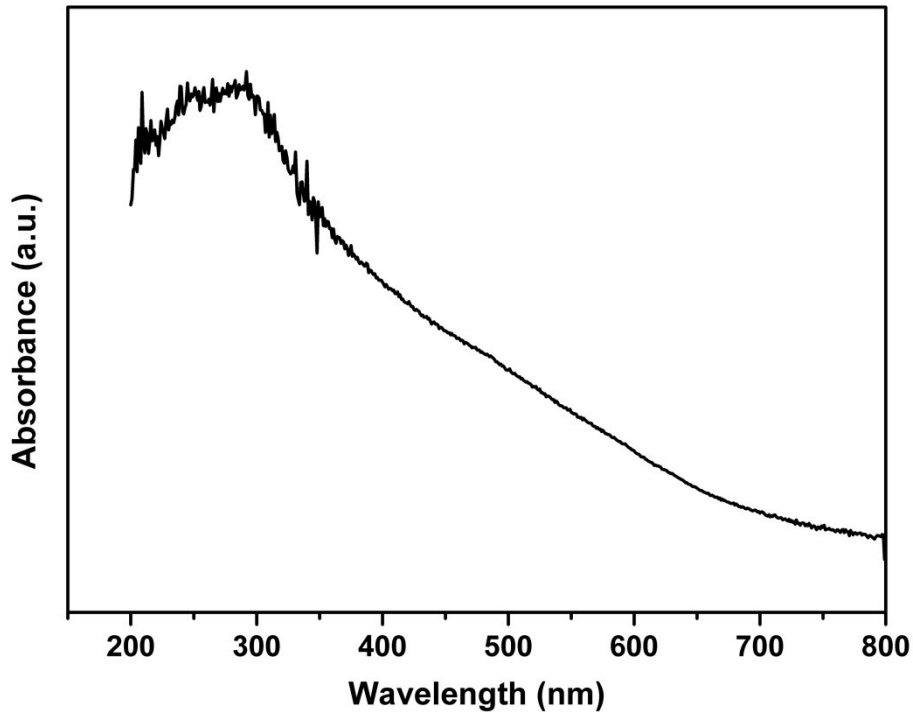

Figure S4. The UV-vis spectrum of the crystal of compound **1**.

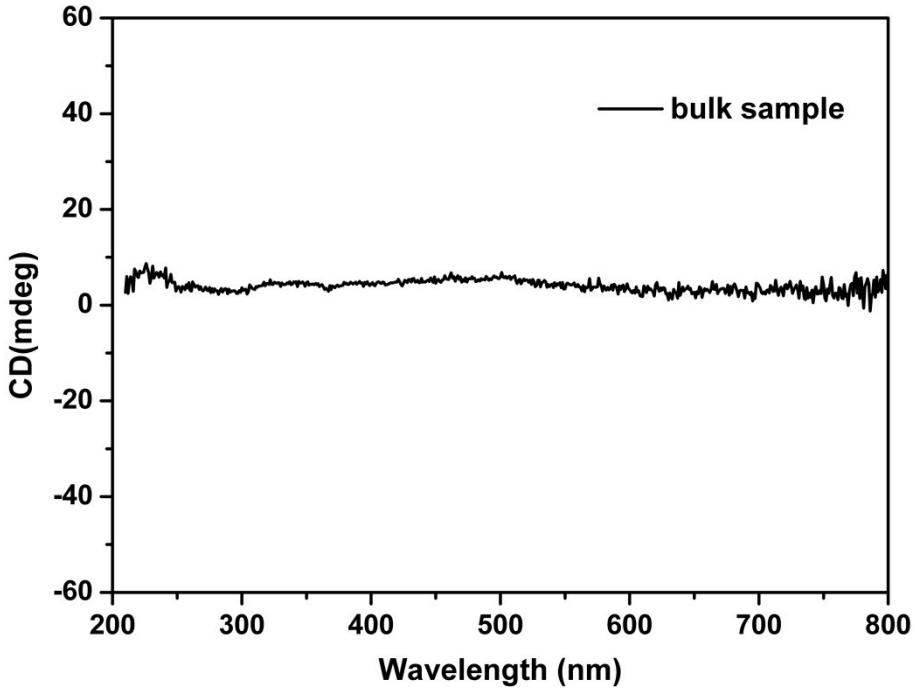

Figure S5. Solid-state CD spectrum of compound **1** (bulk sample). Note: because of the small size and the same appearances of the enantiomers **1R** and **1L**, it is difficult to separate them from one pot synthesis by hand. Therefore, no attempt to get the solid-state circular dichroism spectrum of pure enantiomer **1R** or **1L** was tried. The solid-state circular dichroism (CD) spectra obtained from KCl pellets using all crystals from a single batch proves that overall the expected racemic conglomerate is formed. These results confirm the single-crystal analysis, providing additional evidence for the asymmetric crystallization.

Table S3. A summary of structure determinations of 10 randomly selected crystals in the products of compound **1** from the same crystallization: the *R* factors and Flack absolute structure parameters for each refinement with the same $P4_3$ space group.

	a	*b*	*c*	R_1	wR_2	Flack parameter	Goodness-of-fit on F^2
1	8.704(5)	8.704(5)	37.500(5)	0.0289	0.0865	0.01(3)	1.073
2	8.708(5)	8.708(5)	37.495(5)	0.0319	0.0804	0.01(2)	1.011
3	8.704(5)	8.704(5)	37.498(5)	0.0280	0.0715	0.03(4)	1.008
4	8.709(5)	8.709(5)	37.502(5)	0.0254	0.0616	-0.018(19)	1.018
5	8.710(5)	8.710(5)	37.511(5)	0.0295	0.0599	-0.01(2)	1.061
6	8.713(5)	8.713(5)	37.496(5)	0.0497	0.0858	1.08(4)	1.004
7	8.717(5)	8.717(5)	37.505(5)	0.0334	0.0704	1.00(2)	1.048
8	8.702(5)	8.702(5)	37.521(5)	0.0341	0.0862	0.98(3)	1.021
9	8.720(5)	8.720(5)	37.493(5)	0.0293	0.0680	0.98(2)	1.056
10	8.704(5)	8.704(5)	37.495(5)	0.0262	0.0619	1.05(4)	1.035

In order to further ascertain the spontaneous resolution of this compound, 10 crystals chosen randomly were refined using single crystal X-ray diffraction data under the same space group $P4_3$. The Flack parameters of 5 crystals are close to zero, whereas those of the other 5 are close to one (Table S3, above). When the atomic coordinates of the latter 5 crystals are inverted, the Flack parameters are close to zero (Table S4, below).These results prove spontaneous resolution during the crystallization.

Table S4. A summary of structure determinations of crystals 6-10 with inverted space group $P4_1$.

	a	*b*	*c*	R_1	wR_2	Flack parameter	Goodness-of-fit on F^2
6	8.713(5)	8.713(5)	37.496(5)	0.0351	0.0764	0.002(14)	1.017
7	8.717(5)	8.717(5)	37.505(5)	0.0297	0.0651	-0.022(12)	1.066
8	8.702(5)	8.702(5)	37.521(5)	0.0383	0.0952	0.015(32)	1.078
9	8.720(5)	8.720(5)	37.493(5)	0.0369	0.0712	0.011(27)	1.092
10	8.704(5)	8.704(5)	37.495(5)	0.0232	0.0533	-0.031(17)	1.046

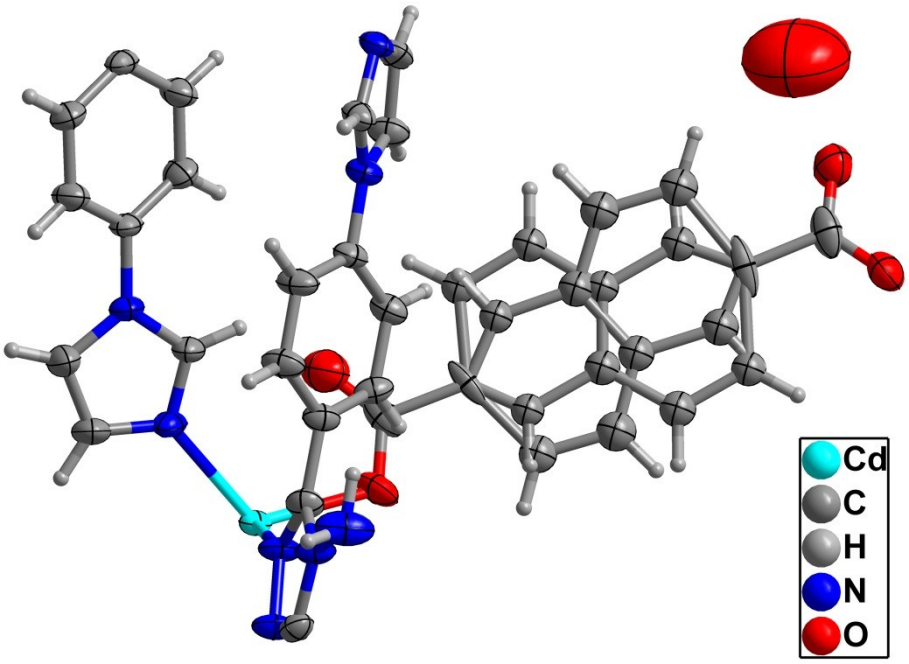

Figure S6. The asymmetric unit of **1R**, with thermal ellipsoids at 50% probability.

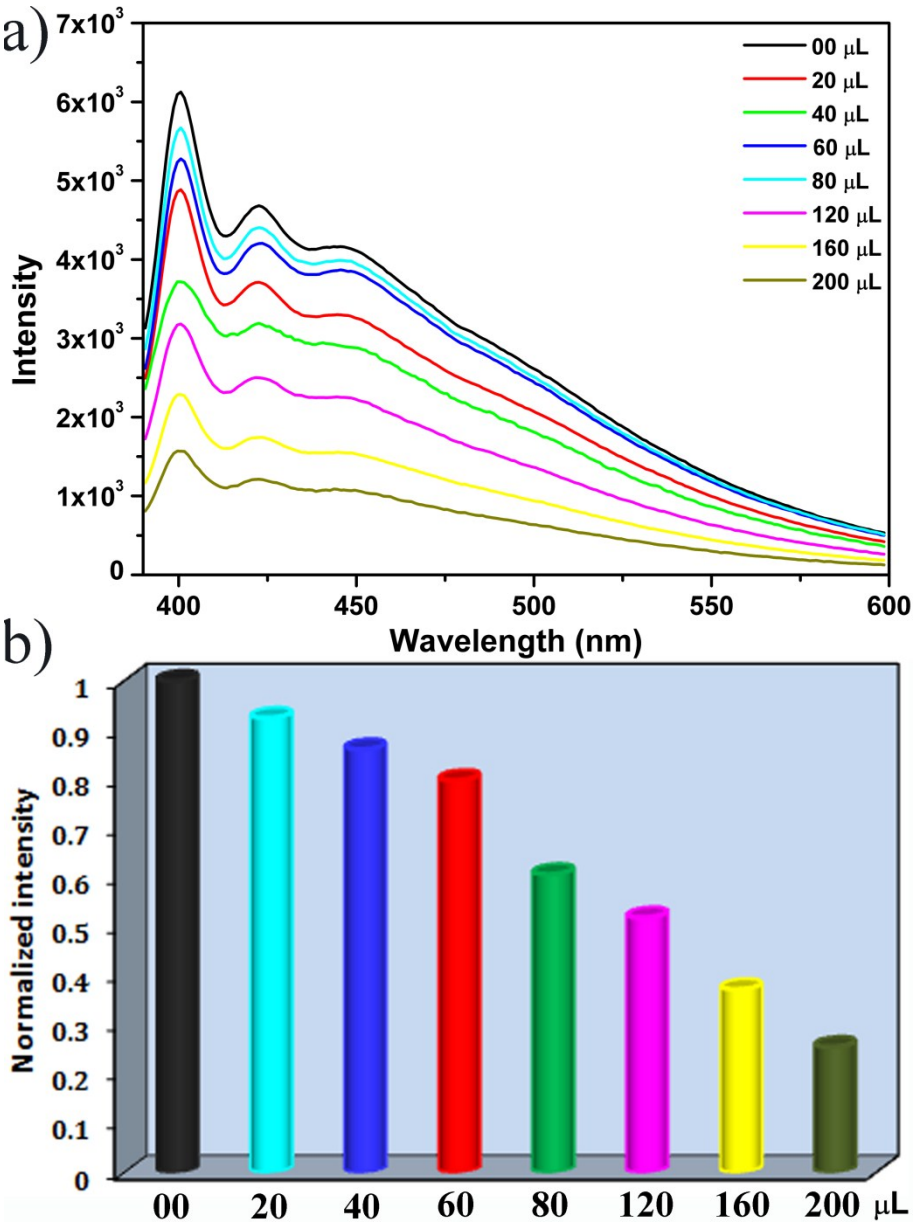

Figure S7. Emission spectra a) and fluorescent intensity changes b) of **1** dispersed in water upon incremental addition of a PA aqueous solution (excited at 370 nm).

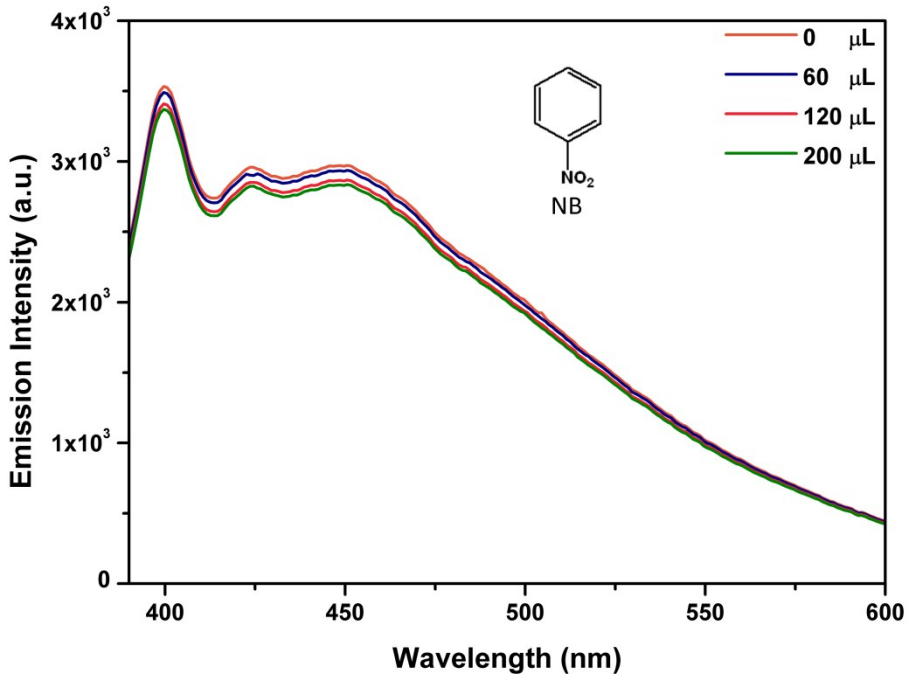

Figure S8. Emission spectra of **1** dispersed in water upon incremental addition of a NB aqueous solution (1mM, excited at 370 nm).

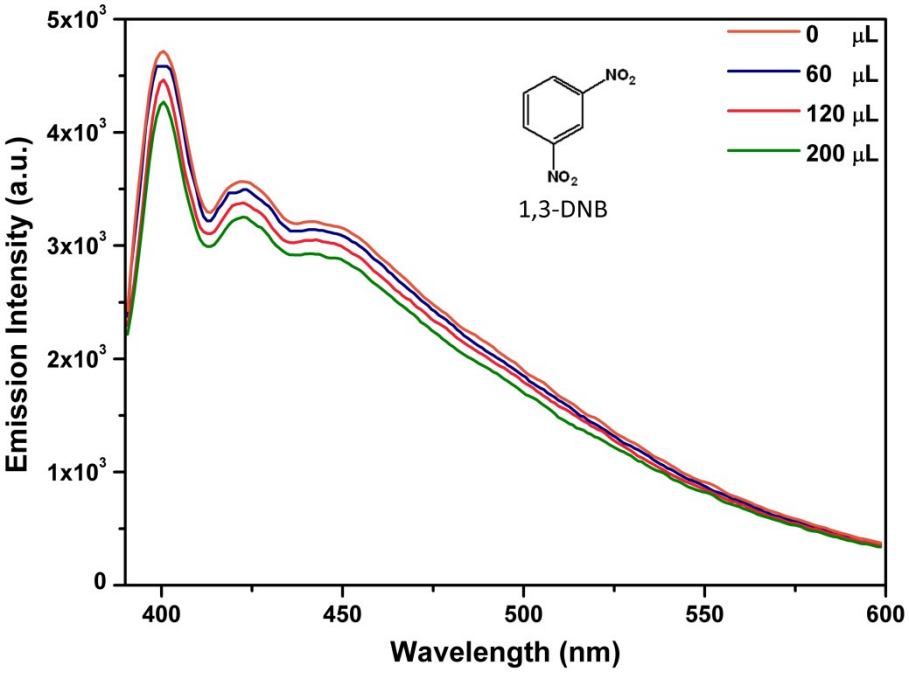

Figure S9. Emission spectra of **1** dispersed in water upon incremental addition of a 1,3-DNB aqueous solution (1mM, excited at 370 nm).

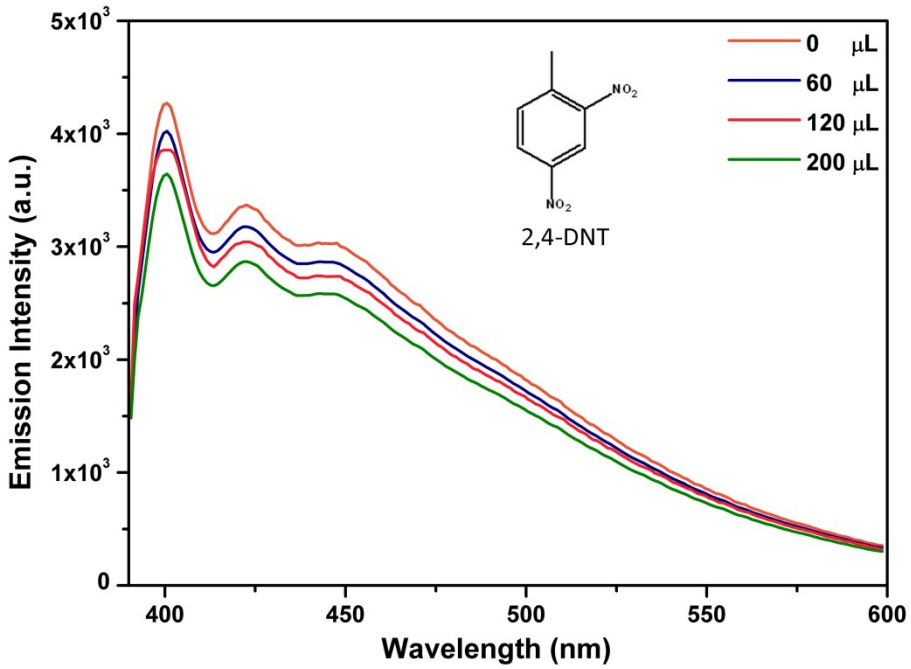

Figure S10. Emission spectra of **1** dispersed in water upon incremental addition of a 2,4-DNT aqueous solution (1mM, excited at 370 nm).

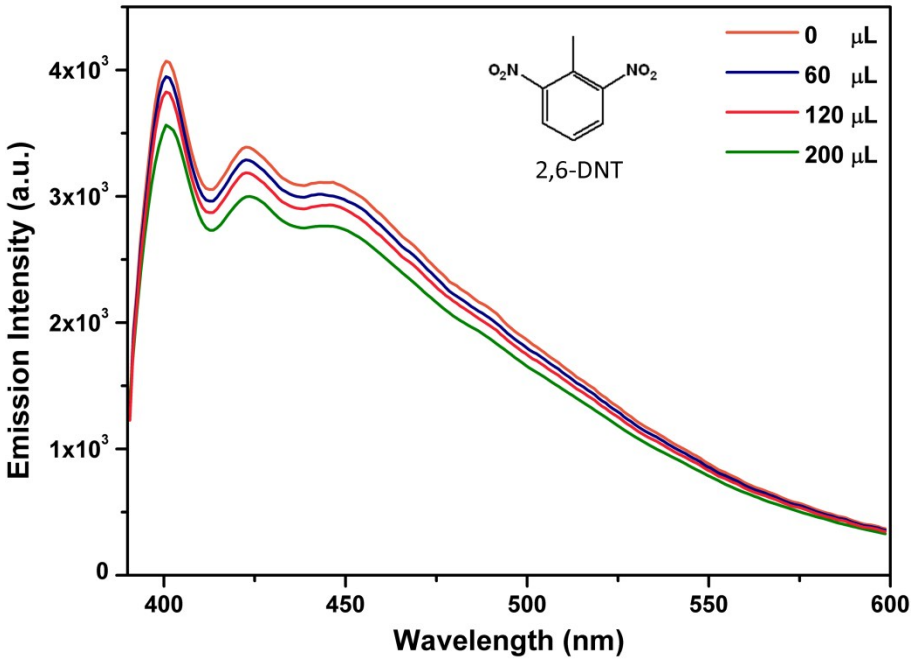

Figure S11. Emission spectra of **1** dispersed in water upon incremental addition of a 2,6-DNT aqueous solution (1mM, excited at 370 nm).

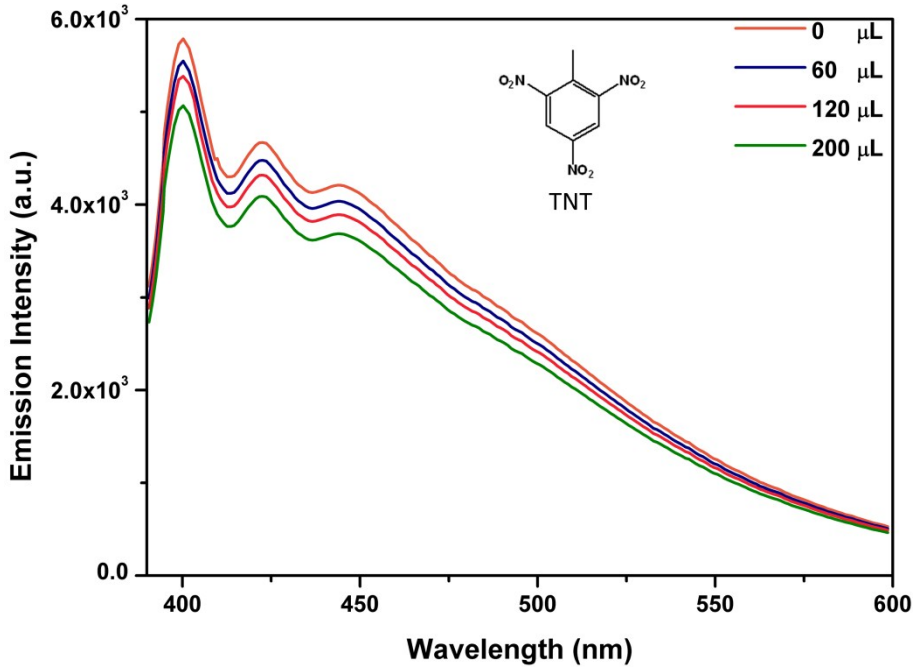

Figure S11. Emission spectra of **1** dispersed in water upon incremental addition of a TNT aqueous solution (1mM, excited at 370 nm).

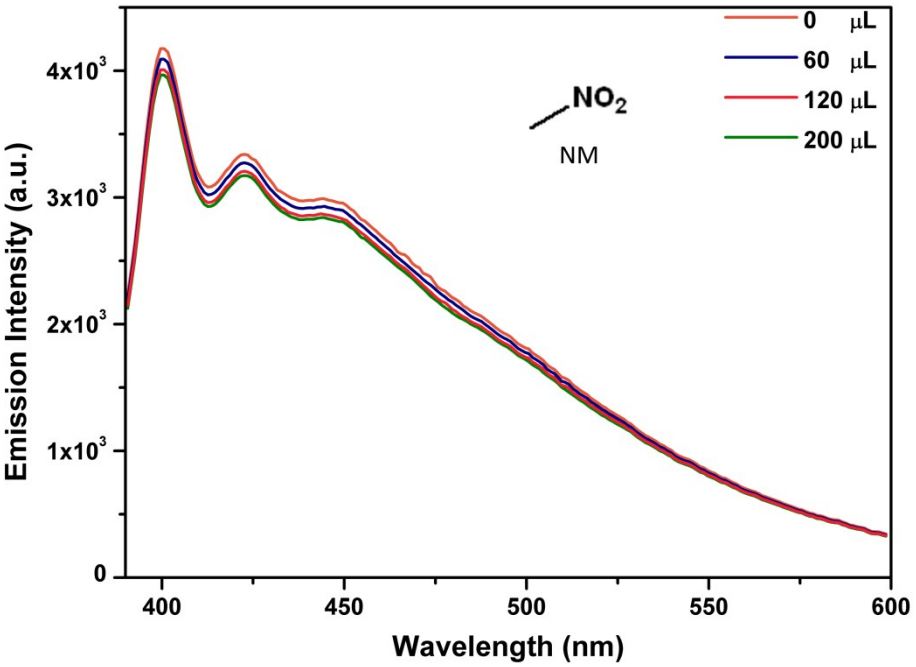

Figure S12. Emission spectra of **1** dispersed in water upon incremental addition of a NM aqueous solution (1mM, excited at 370 nm).

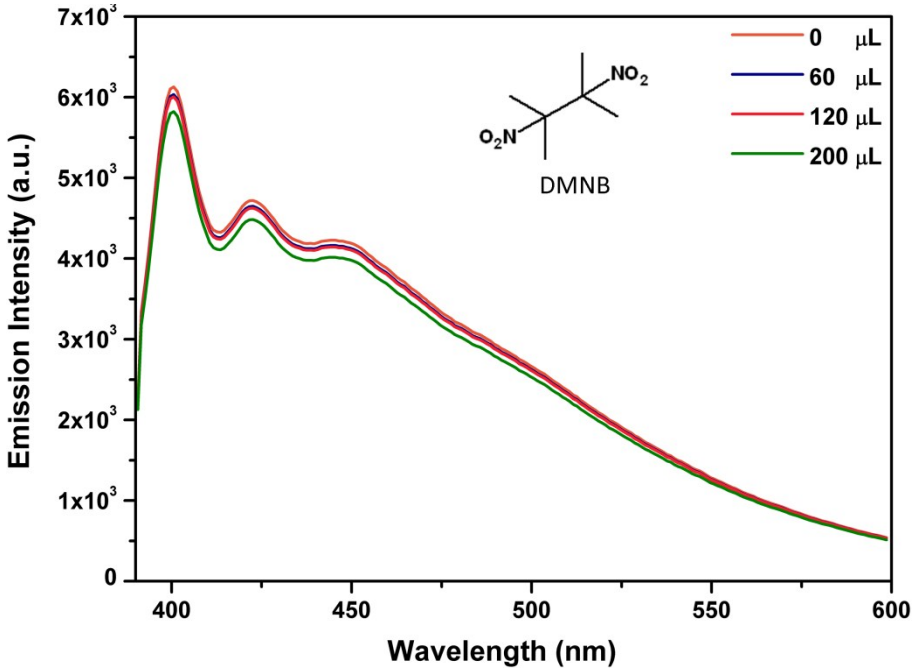

Figure S13. Emission spectra of **1** dispersed in water upon incremental addition of a DMNB aqueous solution (1mM, excited at 370 nm).

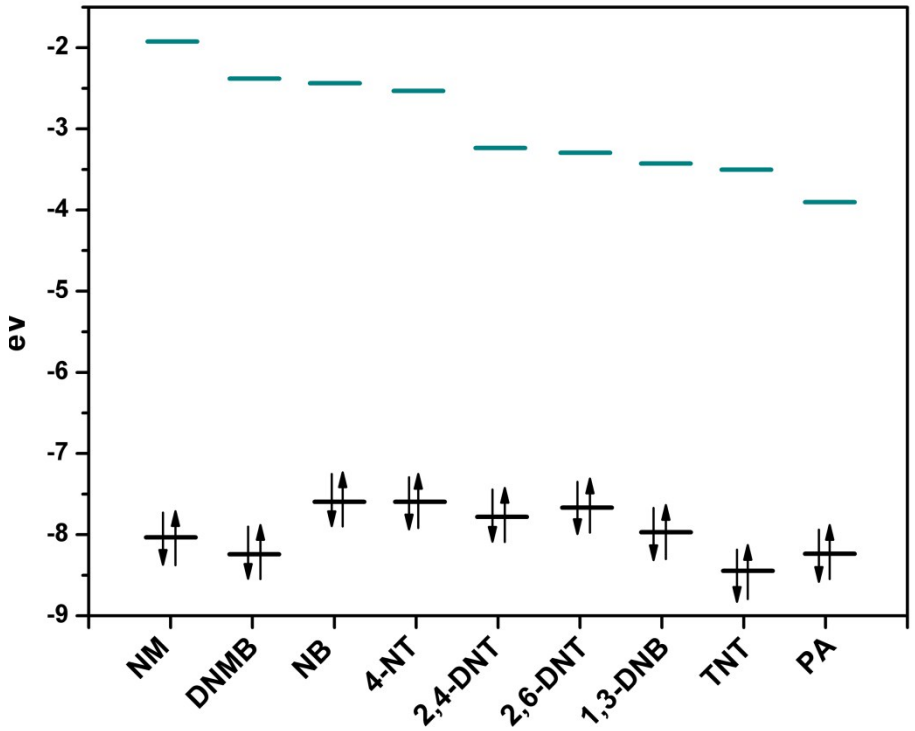

Figure S14. HOMO and LUMO energies of electron deficient nitro compounds.[1]

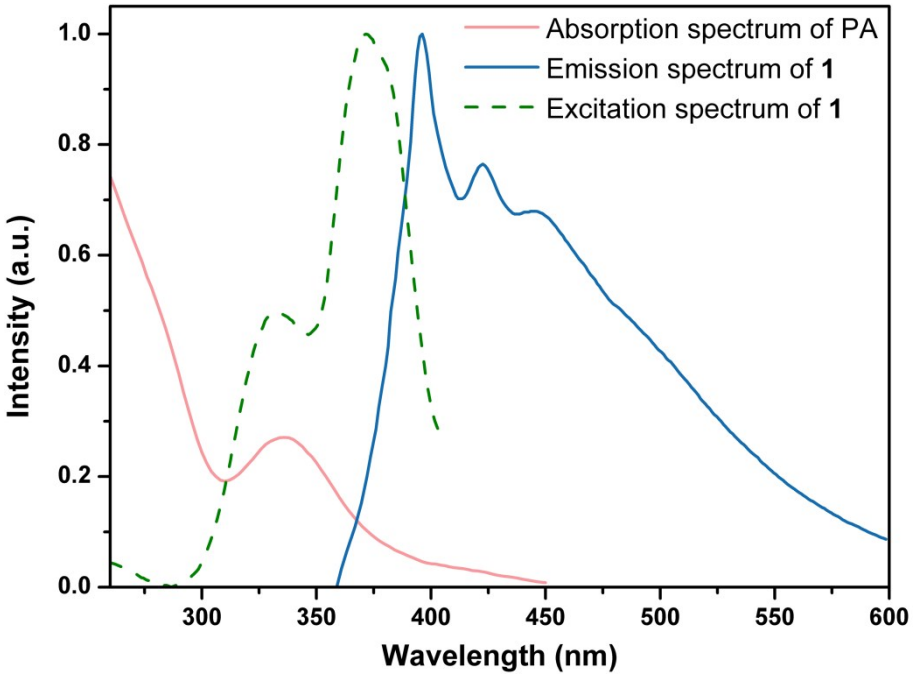

Figure S15. Spectral overlap between normalized absorbance spectra of PA and normalized emission / excitation spectra of **1** in water.

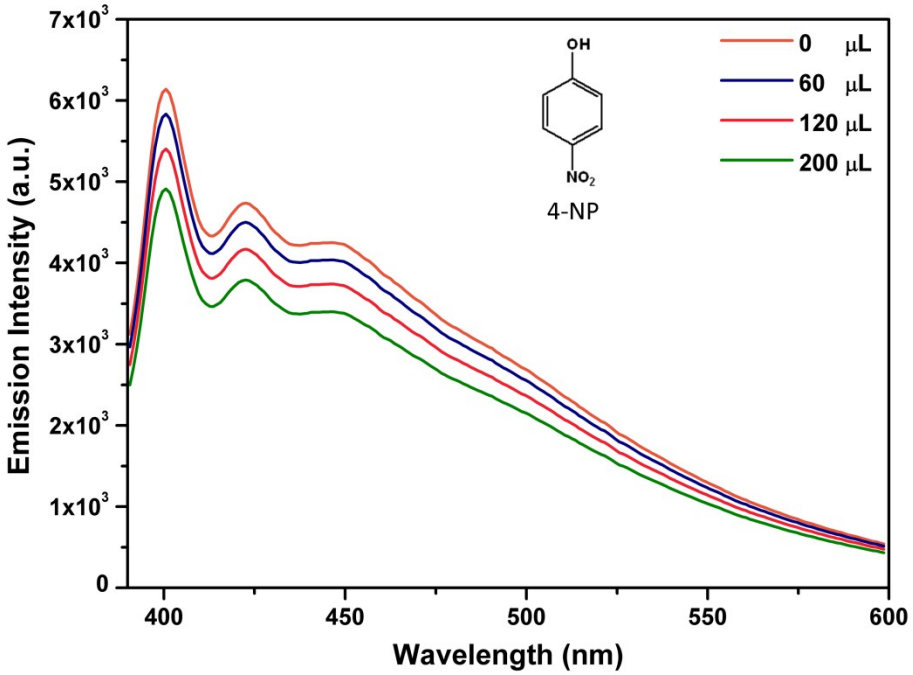

Figure S16. Emission spectra of **1** dispersed in water upon incremental addition of a 4-NP aqueous solution (1mM, excited at 370 nm).

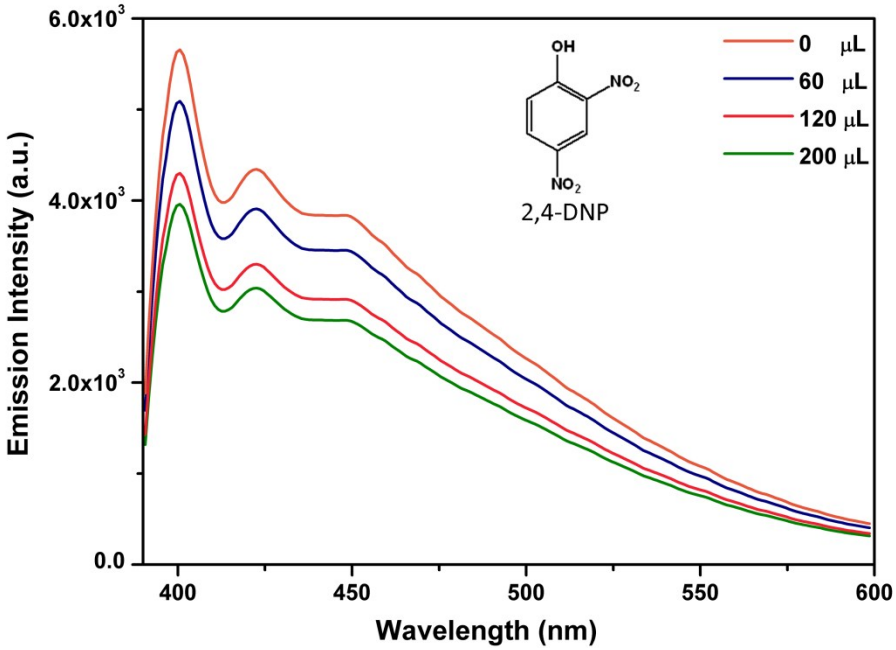

Figure S17. Emission spectra of **1** dispersed in water upon incremental addition of a 2,4-DNP aqueous solution (1mM, excited at 370 nm).

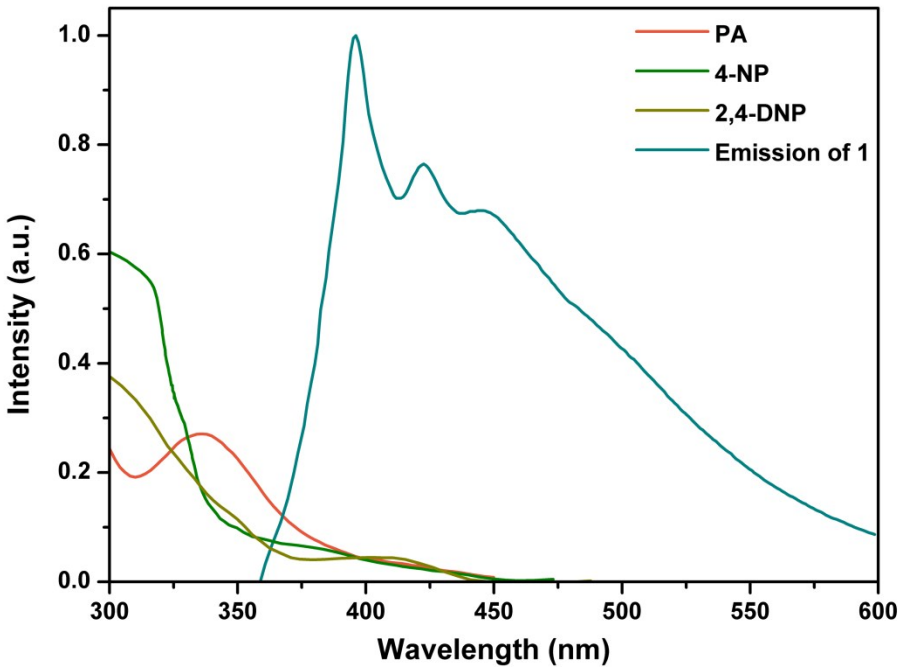

Figure S18. Spectral overlap between normalized absorbance spectra of 4-NP, 2,4-DNP and normalized emission spectra of **1** in water.

References

1 (a) S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem.*, 2013, **125**, 2953-2957; (b) S. Mukherjee, A. V. Desai, A. I. Inamdar, B. Manna and S. K. Ghosh, *Cryst. Growth Des.*, 2015; (c) Y. Peng, A.-J. Zhang, M. Dong and Y.-W. Wang, *Chem. Commun.*, 2011, **47**, 4505-4507; (d) M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543-2555; (e) S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Commun.*, 2014, **50**, 8915-8918; (f) B. Joarder, A. V. Desai, P. Samanta, S. Mukherjee and S. K. Ghosh, *Chem. – Eur. J.*, 2015, **21**, 965-969; (g) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong and J. Li, *Angew. Chem. Int. Ed.*, 2009, **48**, 2334-2338; (h) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153-4155; (i) X.-Z. Song, S.-Y. Song, S.-N. Zhao, Z.-M. Hao, M. Zhu, X. Meng, L.-L. Wu and H.-J. Zhang, *Adv. Funct. Mater.*, 2014, **24**, 4034-4041; (j) D. K. Singha and P. Mahata, *RSC Advances*, 2015, **5**, 28092-28097; (k) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840.