

Electronic Supplementary Information

Supersensitive and selective detection of picric acid explosive by fluorescent Ag nanoclusters

Jian Rong Zhang, Yuan Yuan Yue, Hong Qun Luo,* and Nian Bing Li*

Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education),
School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, PR
China.

* Corresponding authors: linb@swu.edu.cn (N.B. Li); luohq@swu.edu.cn (H.Q. Luo)

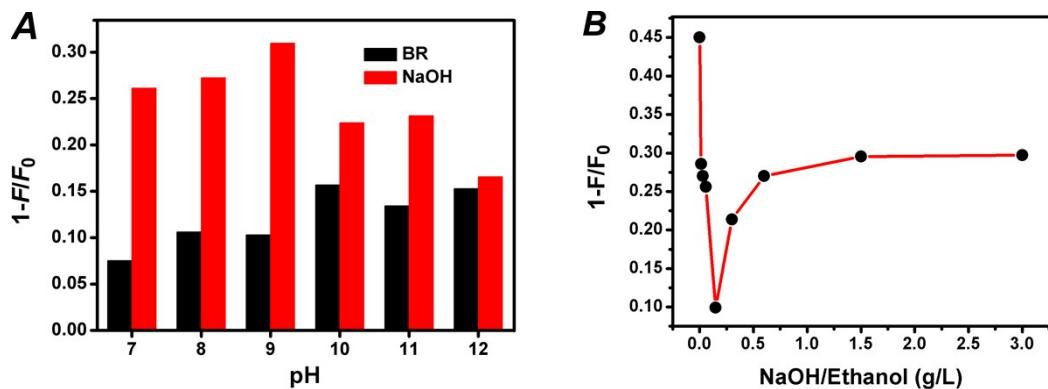


Fig. S1 Fluorescence quenching efficiencies of Ag nanoclusters in different media in the presence of 2 μM PA. Black column in (A) for 10 mM BR buffer solutions at different pHs; red column in (A) for NaOH aqueous solutions at different pHs; (B) for NaOH ethanol solutions with different basicities. F_0 and F represent the fluorescence intensity ($\lambda_{\text{ex}} = 375 \text{ nm}$, $\lambda_{\text{em}} = 450 \text{ nm}$) of Ag nanoclusters in the absence and presence of PA, respectively.

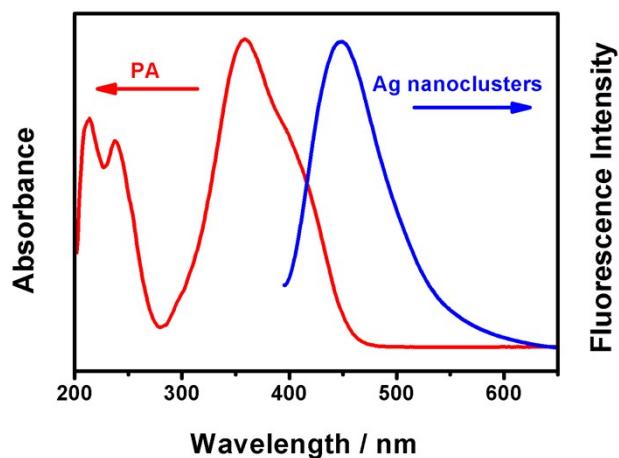


Fig. S2. Absorption spectrum of PA and fluorescence emission spectrum of Ag nanoclusters in ethanol medium.

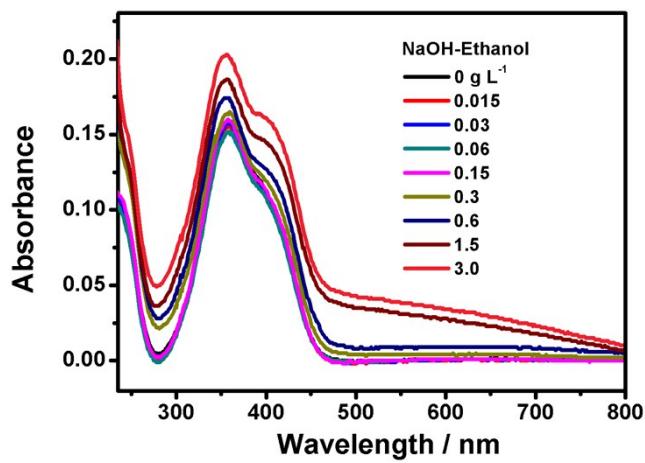


Fig. S3 Absorption spectra of 20 μ M PA in the presence of NaOH ethanol solutions with different basicities. The碱度 (g L^{-1}) of the NaOH ethanol solutions are denoted as grams of NaOH in 1 L ethanol.

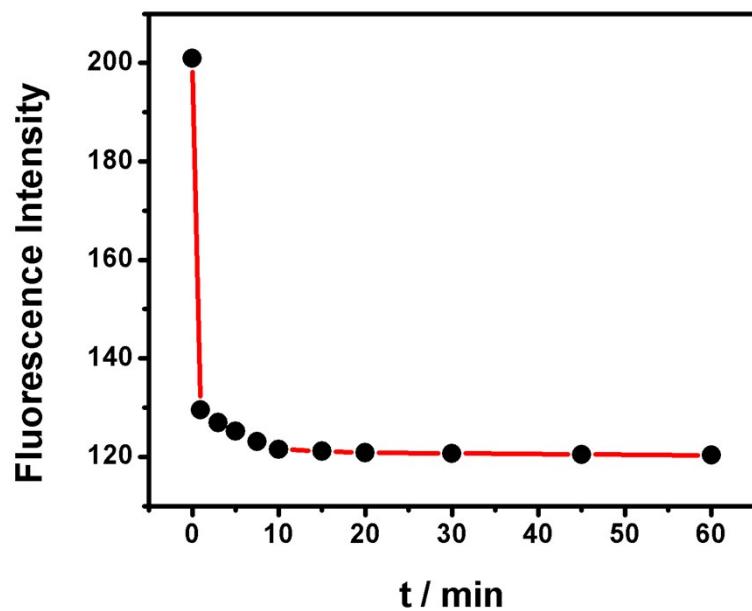


Fig. S4 The fluorescence intensity of Ag nanoclusters in the presence of 2 μM PA after different reaction times in ethanol medium.

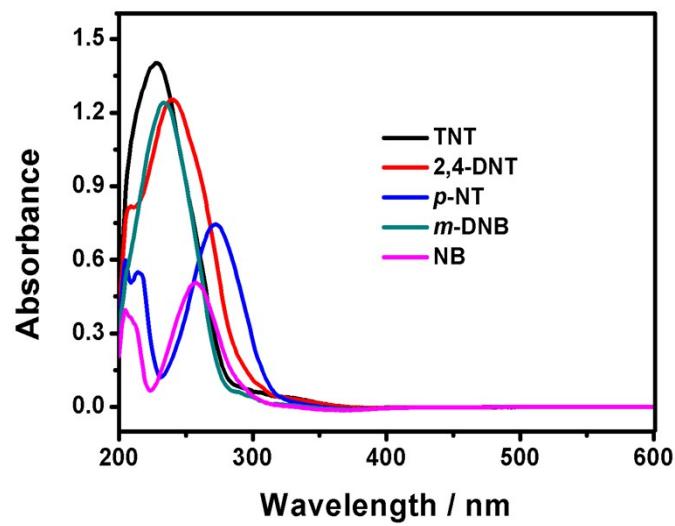


Fig. S5 Absorption spectra of other nitroaromatics in ethanol medium. The concentration of each nitroaromatic is 100 μM .

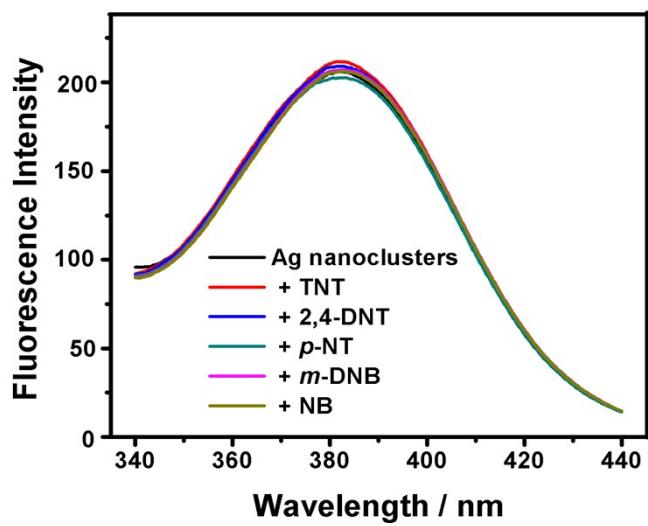


Fig. S6 Excitation spectra of Ag nanoclusters upon addition of different nitroaromatics in ethanol medium. The concentrations of TNT, 2,4-DNT, *p*-NT, *m*-DNB, and NB are 100 μ M, respectively.

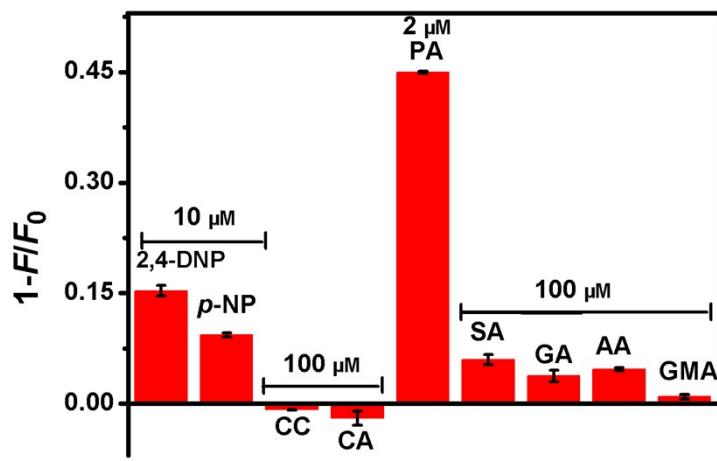


Fig. S7 The fluorescence quenching efficiencies ($1 - F/F_0$) of Ag nanoclusters in the presence of different phenolic compounds and several other acidic and organic analytes in ethanol. The concentration of PA is 2 μM ; the concentrations of 2,4-DNP and *p*-NP are 10 μM , respectively; the concentrations of o-dihydroxybenzene (CC), phenol (CA), salicylic acid (SA), glutaric acid (GA), adipic acid (AA), and L-glutamic acid (GMA) are 100 μM , respectively. F_0 and F denote the fluorescence intensity of Ag nanoclusters in the absence and presence of analyte in ethanol, respectively; $1 - F/F_0$ is the fluorescence quenching efficiency of Ag nanoclusters by analyte.

Table S1 The performance comparison of different fluorescent PA sensors.

Probe ^{ref.}	Medium	Selectivity	Sensitivity (nM)
a conjugated polymer containing heteroatom polycyclic units ¹	CHCl ₃	high	NG
a conjugated polymer film ²	aqueous solution	low	8.7
a composite film of hexaphenylsilole and achitosan ³	water	high	21
photoluminescent polysiloles ⁴	toluene	low	26
an luminogen-functionalized mesoporous material ⁵	water	NG	1.7 × 10 ³
hexa-peri-hexabenzocoronene ⁶	H ₂ O:THF (4:6)	high	4
a pentacenequinone derivative ⁷	toluene:DCM (8:2)	low	350
a mercury-modulated hexaphenylbenzene derivative ⁸	H ₂ O:THF (4:6)	high	30
a pentacenequinone derivative ⁹	H ₂ O:THF (9:1)	low	2.18 × 10 ³
N,N-dimethylaminocinnamaldehyde-Hg ²⁺ complex ¹⁰	THF:H ₂ O (9:1)	high	170
zwitterionic squarainedye ¹¹	CH ₃ CN:H ₂ O (9:1)	high	70
N-acylhydrazone ¹²	DMF	high	430
conjugated asymmetric triazines ¹³	THF/water	high	65
a hetero-oligophenylene derivative ²⁴	H ₂ O:EtOH (6:4)	high	26
electron-rich oligofluoranthene ¹⁵	water	low	10 ⁻³
tris-imidazolium ¹⁶	CHCl ₃	low	NG
p-phenylenevinylene-based molecules ¹⁷	THF/water	high	15.2
(benz)imidazolium based tricationic chemosensors ¹⁸	HEPES buffer : DMSO (98:2)	high	1
pentacenequinone derivatives ¹⁹	H ₂ O:THF (9:1)	low	250
a bispyrene-based molecular ²⁰	Milli-Q water	low	1.0 × 10 ³
boron–dipyrromethene based fluorescence sensor ²¹	CH ₃ CN:H ₂ O (9:1)	high	700
composite films containing oligotriphenylene and oligotriphenylene/polysulfone ²²	Water	low	10
copolymer microspheres of hexachlorocyclotriphosphazene and curcumin ²³	CH ₃ OH	low	370
a metal organic frame ²⁴	CH ₃ CN	high	NG
tryptcene based metal–organic gels ²⁵	ethanol	low	44
Pt ^{II} ₆ nanoscopic cages with an organometallic backbone ²⁶	acetonitrile/chloroform	high	3.4 × 10 ³
8-hydroxyquinoline aluminum-based composite nanospheres ²⁷	phosphate buffer	high	140
polymer functionalized CdTe/ ZnS quantum dots ²⁸	aqueous solution	high	9
graphitic carbon nitride (g-C ₃ N ₄) nanosheets ²⁹	aqueous solution	high	8.2
MoS ₂ quantum dots ³⁰	water	high	95
Ag nanoclusters/DNA hybrids ³¹	phosphate buffer	low	5.2 × 10 ⁻³
polyethyleneimine-capped Ag nanoclusters ^{This Work}	ethanol	high	0.1

NG: Not given

References

- 1 Y. Y. Long, H. B. Chen, H. M. Wang, Z. Peng, Y. F. Yang, G. Q. Zhang, N. Li, F. Liu and J. Pei, *Anal. Chim. Acta* 2012, **744**, 82–91.
- 2 B. W. Xu, X. F. Wu, H. B. Li, H. Tong and L. X. Wang, *Macromolecules* 2011, **44**, 5089–5092.
- 3 G. He, H. N. Peng, T. H. Liu, M. N. Yang, Y. Zhang and Y. Fang, *J. Mater. Chem.* 2009, **19**, 7347–7353.
- 4 S. Honglae, M. C. Rebecca, J. S.; Michael and C. T. William, *Angew. Chem. Int. Ed.* 2001, **40**, 2104–2105.
- 5 D. D. Li, J. Z. Liu, R. T. K. Kwok, Z. Q. Liang, B. Z. Tang and J. H. Yu, *Chem. Commun.* 2012, **48**, 7167–7169.
- 6 V. Vij, V. Bhalla and M. Kumar, *ACS Appl. Mater. Interfaces* 2013, **5**, 5373–5380.
- 7 V. Bhalla, A. Gupta, M. Kumar, D. S. Shankar Rao and S. K. Prasad, *ACS Appl. Mater. Interfaces* 2013, **5**, 672–679.
- 8 V. Bhalla, S. Kaur, V. Vij and M. Kumar, *Inorg. Chem.* 2013, **52**, 4860–4865.
- 9 V. Bhalla, A. Gupta and M. Kumar, *Org. Lett.* 2012, **14**, 3112–3115.
- 10 M. Kumar, S. I. Reja and V. Bhalla, *Org. Lett.* 2012, **14**, 6084–6087.
- 11 Y. Q. Xu, B. H. Li, W. W. Li, J. Zhao, S. G. Sun and Y. Pang, *Chem. Commun.* 2013, **49**, 4764–4766.
- 12 Y. Peng, A. J. Zhang, M. Dong and Y. W. Wang, *Chem. Commun.* 2011, **47**, 4505–4507.

- 13 Z. F. An, C. Zheng, R. F. Chen, J. Yin, J. J. Xiao, H. F. Shi, Y. Tao, Y. Qian and W. Huan, *Chem. Eur. J.* 2012, **18**, 15655–15661.
- 14 S. Kaur, V. Bhalla, V. Vij and M. Kumar, *J. Mater. Chem. C* 2014, **2**, 3936–3941.
- 15 X. G. Li, Y. Z. Liao, M. R. Huang, V. Strong and R. B. Kaner, *Chem. Sci.* 2013, **4**, 1970–1978.
- 16 B. Roy, A. K. Bar, B. Gole and P. S. Mukherjee, *J. Org. Chem.* 2013, **78**, 1306–1310.
- 17 N. Dey, S. K. Samanta and S. Bhattacharya, *ACS Appl. Mater. Interfaces* 2013, **5**, 8394–8400.
- 18 R. Kumar, S. Sandhu, P. Singh, G. Hundal, M. S. Hundal and S. Kumar, *Asian J. Org. Chem.* 2014, **3**, 805–813.
- 19 S. Kaur, A. Gupta, V. Bhalla and M. Kumar, *J. Mater. Chem. C* 2014, **2**, 7356–7363.
- 20 L. P. Ding, Y. M. Bai, Y. Cao, G. J. Ren, G. J. Blanchard and Y. Fang, *Langmuir* 2014, **30**, 7645–7653.
- 21 S. Madhu, A. Bandela and M. Ravikanth, *RSC Adv.* 2014, **4**, 7120–7123.
- 22 Y. Z. Liao, V. Strong, Y. Wang, X. G. Li, X. Wang and R. B. Kaner, *Adv. Funct. Mater.* 2012, **22**, 726–735.
- 23 W. Wei, R. Lu, S. Tang and X. Liu, *J. Mater. Chem. A*, 2015, **3**, 4604–4611.
- 24 S. S. Nagarkar, Bi. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem.* 2013, **125**, 2953–2957.
- 25 S. Barman, J. A. Garg, O. Blacque, K. Venkatesan and H. Berke, *Chem. Commun.*

2012, **48**, 11127–11129.

26 D. Samanta and P. S. Mukherjee, *Dalton Trans.* 2013, **42**, 16784–16795.

27 Y. X. Ma, H. Li, S. Peng and L. Y. Wang, *Anal. Chem.* 2012, **84**, 8415–8421.

28 B. X. Liu, C. Y. Tong, L. J. Feng, C. Y. Wang, Y. He and C. L. Lü, *Chem. Eur. J.*

2014, **20**, 2132–2137.

29 M. Rong, L. Lin, X. Song, T. Zhao, Y. Zhong, J. Yan, Y. Wang, X. Chen,

Anal. Chem. 2015, **87**, 1288–1296.

30 Y. Wang and Y. N. Ni, *Anal. Chem.* 2014, **86**, 7463–7470.

31 N. Enkin, E. Sharon, E. Golub and I. Willner, *Nano Lett.* 2014, **14**, 4918–4922.