Supporting Information

Carbon Dots Fluorescence-Based Colorimetric Sensor for Sensitive Detection of Aluminum Ions with a Smartphone

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Figure S1. (A) Fluorescence spectra and (B) normalized fluorescence spectra of CDs with different concentrations.
Figure S2. Anti-photobleaching property of the CDs when irradiated under UV lamp for 3 hours.

Figure S3. The FTIR spectra of CDs (A) before and (B) after irradiation at 360 nm UV light for 15 mins.
Figure S4. The fluorescence intensity of CDs at different dark storage time interval when irradiated under UV lamp for 15 min once.

Figure S5. TEM images of (A) CDs, (B) CDs with the addition of Al\(^{3+}\) (7.69 mM), the inset shows the distribution histogram of the average diameter of CDs and CDs- Al\(^{3+}\), respectively.

Figure S6. XRD and XPS spectrum of the CDs.
Figure S7. Zeta potential of the CDs and the CDs-Al^{3+} (7.69 mM).

Figure S8. FTIR spectra of (A) CDs, (B-E) CDs with the addition of different concentration of Al^{3+} (7.69 μM, 76.9 μM, 769μM, 7.69 mM).

Figure S9. Fluorescence spectra (A) and I_{500}/I_{420} (B) of CDs after adding 76.92 μM Al^{3+} at the pH from 4.0 to 9.0.
Figure S10. The pH value of different concentrations of Al(NO₃)₃ in acetic-acetate buffer solution (pH 5.0).

Figure S11. Evaluation of the interference from various small molecules in the RGB method. (A) Images of the CDs-Al³⁺ (307.69 μM) solution upon the addition of different small molecule and the mixture of above small molecules obtained with a smartphone under a 360 nm UV lamp. (B) G/B value responses to the different small molecule (307.69 μM glutathione, vitamin C, L-aspartic, fulvic acid, L-glutamic, serine, glucose, L-alanine, glycine, urea, L-threoine and 247 μg/mL humic acid).
### Table S1. Comparison among different methods used in the Al\(^{3+}\) detection.

| Platform/Probe                  | Mechanism                             | Liner range/M | Limit of detection/M | Ref |
|--------------------------------|---------------------------------------|---------------|----------------------|-----|
| Fluorescence method/HL         | ESIPT and PET                         | ---           | 4.0×10\(^{-6}\)      | 1   |
| Fluorescence method/BOS        | CHEF                                  | ---           | 1.855×10\(^{-6}\)   | 2   |
| Fluorescence method/L1         | CHEF                                  | ---           | 8.2×10\(^{-7}\)     | 3   |
| Fluorescence method/CDs        | Surface passivation                   | 0-1.0×10\(^{-5}\) | 3.9×10\(^{-7}\)    | 4   |
| Fluorescence method/L2         | PET                                   | ---           | 7.5×10\(^{-7}\)     | 5   |
| Fluorescence method/HBTP       | ESIPT and CHEF                        | 0-1.2×10\(^{-5}\) | 6.72×10\(^{-8}\) | 6   |
| Fluorescence method/Cys-CuNCs  | AIE                                   | 1.0×10\(^{-6}\) | 2.67×10\(^{-8}\)   | 7   |
| Fluorescence method/(R)-I      | N and O atoms of (R)-I interacting with Al\(^{3+}\) | ---         | 1.4×10\(^{-8}\)   | 8   |
| Fluorescence method/Hmppc      | CHEF                                  | 1.0×10\(^{-6}\) | 4.0×10\(^{-6}\)    | 9   |
| Fluorescence method/L3         | PICT and TICT                         | 1.75×10\(^{-6}\) | 3.3×10\(^{-8}\) | 10  |
| RGB method/CP-ATP              | Interaction of ATP with Al\(^{3+}\)  | 4.0×10\(^{-6}\) | 1.62×10\(^{-10}\)   | 11  |
| Colorimetric method/RB/bis-PDA| Interaction of RB with Al\(^{3+}\)   | 0-9.0×10\(^{-5}\) | 1.8×10\(^{-6}\) | 12  |
| Colorimetric method/IL-AuNPs   | N atoms of IL interacting with Al\(^{3+}\) | ---       | 1.0×10\(^{-6}\) | 13  |
| Colorimetric method/PQTEG      | N atoms of PQTEG interacting with Al\(^{3+}\) | ---       | 8.0×10\(^{-7}\) | 14  |
| Colorimetric method/MMT-AuNP   | N atoms of MMT–AuNP interacting with Al\(^{3+}\) | 1.0×10\(^{-6}\) | 5.3×10\(^{-7}\) | 15  |
| Colorimetric method/TTP-AuNPs  | Triazole–ether interacting with Al\(^{3+}\) | 5.0×10\(^{-7}\) | 1.8×10\(^{-6}\) | 16  |
| Colorimetric method/H          | O atoms of H interacting with Al\(^{3+}\) | 0-3.0×10\(^{-5}\) | 1.42×10\(^{-8}\) | 17  |
| Colorimetric method/J-AgNPs    | O atoms of J-AgNPs interacting with Al\(^{3+}\) | 1.0×10\(^{-7}\) | 1.0×10\(^{-8}\) | 18  |
| Fluorescence method/CDs        | O atoms of CDs interacting with Al\(^{3+}\) | 1.54×10\(^{-7}\) | 1.138×10\(^{-7}\) | This work |
| RGB method/CDs                 | O atoms of CDs interacting with Al\(^{3+}\) | 1.54×10\(^{-5}\) | 5.55×10\(^{-6}\) | This work |

HL: 2-hydroxy-1-naphthylaldehyde nicotinoyl hydrazone
BOS: rhodamine B-based chromo-fluorogenic probe
L1: 8-formyl-7-hydroxyl-4-methyl coumarin-(20-methylquinoline-4-formyl) hydrazone
L2: 2-hydroxy-5(4-nitrophenyl)diiazole benzaldehyde-appended rhodamine based scaffold
HBTP: pyridine conjugated hydroxybenzothiazole
Cys-CuNCs: Cysteamine-capped copper nanoparticles
(R)-1: (2R,20R)-2,2’-(1,3-phenylenebis(methylene))bis(pyren-1-ylmethyl)azanediyi)bis(2-phenylethanol-1-ol)
Hmppc: 5-methyl-1- pyridin-2-yl-1H-pyrazole-3-carboxylic acid (1-pyridin-2-yl-ethylidene)-hydrazone
L3: (5-{[(4-diethylamino-2-hydroxy-benzylidene)-amino]-1H-pyrimidine-2, 4-dione)
CP-ATP: copolymer-ATP
RB/bis-PDA film: rhodamine B-functionalized bis-polydiacytylene film
IL-AuNPs: 1-ethyl-3-methylimidazolium thiocyanate-coated gold nanoparticles
PQTEG: (2-(2-hydroxyethoxy)ethoxy)ethyl 8-propoxyquinoline-2-carboxylate
MMT–AuNP: 5-mercaptomethyltetrazole- gold nanoparticles
TTP–AuNPs: triazole-ether functionalized gold nanoparticles
H: the organic-inorganic nanohybrid by immobilization of AuNPs on organic nanoparticles
J-AgNPs: the bifunctional Jamun stabilized silver nanoparticles
ESIPT: excited state intramolecular proton transfer mechanism; PET: photo-induced electron transfer; CHEF: chelation-enhanced fluorescence; AIE: aggregate-induced emission; PICT: normal planar intramolecular charge transfer; TICT: twisted intramolecular charge transfer.

References

1. Qin, J.C.; Yang, Z.Y.; Yang, P. Recognition of Al³⁺ based on a naphthalene-based “off-on” chemosensor in near 100% aqueous media. *Inorg. Chem. ACTA* 2015, 432, 136-141. https://doi.org/10.1016/j.ica.2015.03.029.

2. Leng, X.; Jia, X.; Qiao, C.F.; Xu, W.F.; Ren, C.T.; Long, Y.; Yang, B.Q. Synthesis, characterization and Al³⁺ sensing application of a new chromo-fluorogenic chemosensor. *J. Mol. Struct.* 2019, 1193, 69-75. https://doi.org/10.1016/j.molstruc.2019.05.032.

3. Qin, J.C.; Li, T.R.; Wang, B.D.; Yang, Z.Y.; Fan, L. Fluorescent sensor for selective detection of Al³⁺ based on quinoline-coumarin conjugate. *Spectrochim. ACTA A* 2014, 133, 38-43. https://doi.org/10.1016/j.saa.2014.05.033.

4. Sun, X.Y.; Wu, L.L.; Shen, J.S.; Cao, X.G.; Wen, C.J.; Liu, B.; Wang, H.Q. Highly selective and sensitive sensing for Al³⁺ and F⁺ based on green photoluminescent carbon dots. *RSC Adv.* 2016, 6, 97346-97351. https://doi.org/10.1039/c6ra19370f.

5. Gupta, V.K.; Singh, A.K.; Kumawat, L.K. Thiazole Schiff base turn-on fluorescent chemosensor of Al³⁺ ion. *Sensor. Actuat. B-Chem.* 2014, 195, 98-108. https://doi.org/10.1016/j.snb.2013.12.092.

6. Das, S.; Goswami, S.; Aich, K.; Ghoshal, K.; Quah, C.K.; Bhattacharyya, M.; Fun, H.K. ESIPT and CHEF based highly sensitive and selective ratiometric sensor for Al³⁺ with imaging in human blood cell. *New J. Chem.* 2015, 39, 8582-8587. https://doi.org/10.1039/c5nj01468a.

7. Boonmee, C.; Promarak, V.; Tuntulani, T.; Ngeontae, W. Cysteamine-capped copper nanoclusters as a highly selective turn-on fluorescent assay for the detection of aluminum ions. *Talanta* 2018, 178, 796-804. https://doi.org/10.1016/j.talanta.2017.10.006.

8. Prabhuj, J.; Velumurugan, K.; Raman, A.; Duraipandy, N.; Kiran, M.S.; Easwaramoorthi, S.; Tang, L.J.; Nandhakumar, R. Pyrene-phenylglycinol linked reversible ratiometric fluorescent chemosensor for the detection of aluminium in nanomolar range and its bio-imaging. *Anal. Chim. ACTA* 2019, 1090, 114-124. https://doi.org/10.1016/j.aca.2019.09.008.

9. Naskar, B.; Das, K.; Mondal, R.R.; Maiti, D.K.; Requena, A.; Ceron, C.J.P.; Prodhan, C.; Chaudhuri, K.; Goswami, S. A new fluorescence turn-on chemosensor for nanomolar detection of Al³⁺ constructed from pyridine-pyrazole system. *New J. Chem.* 2018, 42, 2933-2941. https://doi.org/10.1039/c7nj03955g.
10. Upadhyay, K.K.; Kumar, A. Pyrimidine based highly sensitive fluorescent receptor for Al\textsuperscript{3+} showing dual signalling mechanism. Org. Biomol. Chem. 2010, 8, 4892-4897. https://doi.org/10.1039/c0ob00171f.

11. Tu, M.C.; Rajwar, D.; Ammanath, G.; Alagappan, P.; Yildiz, U.H.; Liedberg, B. Visual detection of Al\textsuperscript{3+} ions using conjugated copolymer-ATP supramolecular complex. Anal. Chim. ACTA 2016, 912, 105-110. https://doi.org/10.1016/j.aca.2015.12.002.

12. Wang, H.; Han, S.H. Bis-ratiometric absorbance detection of Al(III) in the rhodamine B-functionalized bis-polydiacetylene film. Chem. Pap. 2017, 71, 2129-2137. https://doi.org/10.1007/s11696-017-0205-9.

13. Chen, W.W.; Jia, Y.X.; Feng, Y.; Zheng, W.S.; Wang, Z.; Jiang, X.Y. Colorimetric detection of Al(III) in vermicelli samples based on ionic liquid group coated gold nanoparticles. RSC Adv. 2015, 5, 62260-62264. https://doi.org/10.1039/c5ra09099g.

14. Jisha, B.; Resmi, M.R.; Maya, R.J.; Varma, R.L. Colorimetric detection of Al(III) ions based on triethylene glycol appended 8-propyloxy quinoline ester. Tetrahedron Lett. 2013, 54, 4232-4236. https://doi.org/10.1016/j.tetlet.2013.05.134.

15. Xue, D.S.; Wang, H.Y.; Zhang, Y.B. Specific and sensitive colorimetric detection of Al\textsuperscript{3+} using 5-mercaptomethyltetrazole capped gold nanoparticles in aqueous solution. Talanta 2014, 119, 306-311. https://doi.org/10.1016/j.talanta.2013.11.012.

16. Chen, Y.C.; Lee, I.L.; Sung, Y.M.; Wu, S.P. Colorimetric detection of Al\textsuperscript{3+} ions using triazole–ether functionalized gold nanoparticles. Talanta 2013, 117, 70-74. https://doi.org/10.1016/j.talanta.2013.08.054.

17. Kaur, R.; Kaur, N.; Kuwar, A.; Singh, N. Colorimetric sensor for detection of trace level Al(III) in aqueous medium based on organic-inorganic nanohybrid. Chem. Phys. Lett. 2019, 722, 140-145. https://doi.org/10.1016/j.cplett.2019.03.014.

18. Painuli, R.; Joshi, P.; Kumar, D. Cost-effective synthesis of bifunctional silver nanoparticles for simultaneous colorimetric detection of Al(III) and disinfection. Sensor. Actuat. B-Chem. 2018, 272, 79-90. https://doi.org/10.1016/j.snb.2018.05.131.

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