The Inherent Relationship between Carbon Nanodots and Carbon Source in the Determination of Metal Ions

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Research Article

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Abstract

Carbon nanodots (CDs) have exhibited excellent sensing capability for various metal ions. However, it is difficult to determine the selectivity of CDs to metal ions. In this work, we chose appropriate carbon source to design CD sensors against Cu(II) and Ag(I). Glycine, histidine and leucine have been confirmed to form complexes with Cu(II) and Ag(I), and were applied to prepare CDs using microwave heating method. The as-prepared CDs inherited the specific ion-binding capability from their carbon source and could response to both Cu(II) and Ag(I). The response sensitivity corresponded to the binding energy between the carbon source and metal ions. These experimental results are very important for the further design of CD sensors for a large variety of analytes.

Introduction

Carbon nanodots (CDs) are one of the most widely researched fluorescence nanomaterials. Compared with other fluorescence nanomaterials, CDs are particular in their stable photoluminescence (PL) performance, green synthetic methods, abundant raw materials, as well as good biocompatibility [1–3]. Fluorescent CDs can be applied in many research fields, especially in environmental and biomedical sensing applications. CDs are sensitive to a list of analytes in solution, including small organic molecules and bio-macromolecules [4–6]. PL turn-on or turn-off phenomenon appears and can be utilized to realize the qualitative and quantitative analysis of various analytes.

Interestingly, CDs are born to be the fluorescent sensors of various metal ions. Almost all of the CDs can response to one or several kinds of metal ions. The metal ion sensors based on CDs are reliable and accurate, with a high stability and sensitivity. However, there are still two problems demanding to be resolved immediately for the CD sensors. The first problem is about the sensing mechanism of CD for various metal ions, which is indefinite and requires further research and discussion [7]. Two mechanisms are widely accepted, one of which is the fluorescence inner filter effect [8, 9] and the other is the binding induced energy transfer between metal ions and CDs [10, 11]. The second problem appears in the design of CD sensors. Most of the current CD sensors for metal ions were born through later screening methods. In simple words, CDs were prepared first from various carbon source, and then the ion selectivity was determined through contrasting the fluorescence variation of CDs in the presence of various metal ions. These two problems limit the development of CD sensors. This research is focused on the second problem.

In fact, most of the sensors are designed through a classical lock-and-key approach inspired by nature. The sensing process is accomplished through the specific interaction between sensors and analytes, just like a lock and a key. In order to realize the specific recognition, the sensors must be designed with special structure or functional groups to selectively bind with analytes. The lock-and-key approach gives us a clue to design CD sensors. CDs are prepared from carbon source and can inherit some important structural characters or functional groups from carbon source. Therefore, it is possible to control the ion
selectivity of CDs through choosing appropriate carbon source, which has specific binding capacity with certain metal ions.

Amino acids have been confirmed to form stable complexes with Ag(I) and Cu(II) [12–16]. Herein, in this research, Ag(I) and Cu(II) sensors based on CDs were designed through choosing amino acids as carbon source. The inherent relationship between CDs and carbon source in the determination of metal ions was investigated and discussed. Three kinds of amino acids, including glycine (Gly), histidine (His) and leucine (Leu), were chosen to prepare CDs. Experimental results showed that all these CDs were sensitive to both Ag(I) and Cu(II). Moreover, the detection sensitivity depends on the binding energy of the carbon source to various metal ions. Scheme 1 shows the synthetic procedures of CDs, as well as their sensing mechanism to metal ions.

**Experimental**

**Materials**

Urea, glycine, histidine and leucine were ordered from InnoChem Science&Technology Co. Ltd. (Beijing, China). All the chemicals were used directly without further purification. Dialysis bag was ordered from Baoman Biological technology Co. Ltd. (Shanghai, China). Ultrapure water was used throughout all experiments.

**Instruments**

Photoluminescence (PL) measurements were recorded by RF-5301PC (Shimadzu, Japan). Both the excitation and emission slits were set as 3 and 3 nm, respectively. PL spectra were processed using normalized method, and the normalized fluorescence intensity was obtained through dividing each PL intensity of the PL spectra by the maximum value of their own. Microwave reactions were carried out using a domestic microwave oven with the power of 750 W.

**Synthesis of G-CDs, H-CDs and L-CDs**

All of the CDs were prepared using a microwave irradiation method in our previous work [6]. In a typical procedure, 4.0 mmol amino acid and 16.7 mmol urea were dissolved in 10 mL ultrapure water. The mixed solution was heated in a microwave oven for 4 min, and then crude CD powder was gotten. The resultant solid powder was re-dissolved in 10 mL ultrapure water to prepare CD solution. The CD solution was centrifuged at 12 000 rpm for 4.5 min to remove insoluble impurities. The supernatant was then dialyzed against ultrapure water using a dialysis bag (molecular weight cutoff = 8 000–14 000) for 48 hours to remove residual reactants and precursors. The resultant dialysate was freeze-dried and finally brown CD powder was collected. The CDs prepared from glycine, histidine and leucine were called as G-CDs, H-CDs and L-CDs, respectively.

**PL Assay of Metal Ions**
The PL spectra of CDs were followed in the presence of various metal ions with a certain concentration. In order to minimize the interference of CD concentration, the absorbance of CD solution was calibrated to 0.1. On this basis, a definite volume of metal-ion solution (0.5 mL) with various calculated concentrations was added into CD solution (3.5 mL). The PL of the as-prepared CDs were all excitation-depended. The PL spectra of the CD solution were recorded at the optimal excitation wavelength, where the PL intensity of CD can reach the maximum.

Results And Discussions

Characterization of CDs

The morphology of the CDs can be observed in HR-TEM images. Typical spherical CDs are presented in Fig. 1, with an average diameter of about 10 nm. DLS tests reveal that the as-prepared CDs possess a good size distribution, and the size results keep pace with those from the TEM tests. The PL of the as-prepared CDs are typically excitation-dependent due to the quantum confinement [17, 18]. With the gradual increase of excitation wavelength from 310 to 390 nm, the fluorescence intensity increases first and then decreases after reaching a maximum value, while the emission wavelength is gradually red-shifted (Fig. 2). The optimal excitation wavelength ($\lambda_{ex}$) of these three CDs, as well as its corresponding maximum fluorescence emission wavelength ($\lambda_{em}$), is slightly different (G-CDs: $\lambda_{ex} = 330$ nm, $\lambda_{em} = 380$ nm; H-CDs, $\lambda_{ex} = 350$ nm, $\lambda_{em} = 425$ nm; L-CDs: $\lambda_{ex} = 350$ nm, $\lambda_{em} = 420$ nm). All of the CDs show a relatively high fluorescence quantum yield (G-CDs: 15.69%; L-CDs: 17.19%; H-CDs: 10.32%).

PL Assay of Metal Ions

In order to evaluate the metal ion selectivity of CDs, the PL spectra of CDs were monitored in the presence of various metal ions with the same concentration, including Al(III), Ba(II), Ca(II), Cr(III), Mn(II), Pb(II), Hg(II), Ni(I), Co(II), Fe(III), Cu(II), and Ag(I). Results revealed that all of the CDs showed fluorescence fluctuation in varying degrees in the presence of various metal ions (Fig. 3). Most of the metal ions lead to the fluorescence quenching of the CDs. The response was caused by the complicated interaction between the CDs and metal ions, including electrostatic interaction and coordination effect. There exist carboxyl, amino, and hydroxyl groups on the surface of CDs [19–21]. The negative carboxyl groups of CDs can electrostatically bind with metal cations [22]. In this respect, the fact that all of the metal ions could have an effect on the CDs is easy to understand. However, the significant influence in the variation of fluorescence intensity should originate from the specific coordination effect [23–25]. Among these given metal ions, only Fe(III), Cu(II), and Ag(I) had significant effects on the CDs. Many CDs have been reported to be sensitive to Fe(III), due to their oxygen-contained functional groups coordinated with Fe(III) [26, 27]. Cu(II) or Ag(I) responsive CDs have also been reported in some research, respectively [28–31]. However, there are hardly any literatures about the CDs sensitive to both Cu(II) and Ag(I), simultaneously. Therefore, the particular response should depend on the carbon source we chose to prepare CDs. Gly, His and Leu have been confirmed to form stable coordination complexes with Cu(II) and Ag(I) [32–37]. The CDs prepared from these three amino acids could also inherit the coordination capability.
In order to investigate the inherent relationship between the CDs and their corresponding carbon source in the determination of metal ions, we also monitored the fluorescence intensity of CDs with the variation of Cu(II) and Ag(I) concentration (Fig. 4). With the increase of Cu(II) and Ag(I) concentration, the fluorescence intensity of CDs decreased regularly (Fig. 5). There existed a good linear relationship between the fluorescence intensity of CDs and the concentration of metal ions in the range of low concentrations. Afterwards, the fluorescence intensity of CDs tended to be constant, indicating that the binding of metal ions reached a saturated state. Comparatively speaking, the fluorescence intensity of H-CDs quenched more compared with the other two CDs, and L-CDs took the second place. The fluorescence quenching degree of CDs can reflect their sensitivity to metal ions. Therefore, among these three CDs, H-CDs are the most sensitive CDs to Cu(II) and Ag(I); L-CDs comes second. Moreover, the sensitivity of the CDs to Ag(I) and Cu(II) keeps pace with the binding ability of their corresponding amino-acid carbon source with Ag(I) and Cu(II). The binding ability between amino acids and metal ions can be evaluated through calculating their binding energy, which have been reported in some literatures [38–40]. Table 1 shows the binding energies of different amino acids to silver and copper [13], and the binding energy is Gly < Leu < His.
**Table 1**  
Relative binding energies (kcal/mol) of amino acids to silver(I), copper(II) and the proton[13]

| Amino acid | $\Delta G^\circ_{Ag}$[a] | $\Delta H^\circ_{Cu}$ | $\Delta GB$ |
|------------|-------------------------|----------------------|-------------|
| Gly(G)     | 0.0                     | 0.0                  | 0.0         |
| Ala(V)     | 1.4 ± 0.0               | 1.7                  | 3.7         |
| Val(V)     | 2.4 ± 0.2               | 3.7                  | 5.8         |
| Leu(L)     | 2.5 ± 0.1               | 4.1                  | 6.8         |
| Ile(I)     | 2.8 ± 0.0               | 4.3                  | 7.6         |
| Asp(D)     | 3.0 ± 0.2               | 5.0                  | 5.4         |
| Ser(S)     | 3.2 ± 0.4               | 3.1                  | 6.8         |
| Thr(T)     | 4.6 ± 0.1               | 4.6                  | 8.8         |
| Glu(E)     | 4.6 ± 0.1               | 7.2                  | 6.4         |
| Pro(P)     | 5.0 ± 0.1               | 4.8                  | 8.1         |
| Asn(N)     | 8.3 ± 0.3               | 6.7                  | 9.4         |
| Phe(F)     | 9.5 ± 0.3               | 8.0                  | 8.8         |
| Tyr(Y)     | 9.6 ± 0.1               | 8.3                  | 9.6         |
| Gln(Q)     | 10.7 ± 0.2              | 9.8                  | 11.4        |
| Met(M)     | 13.1 ± 0.1              | 10.4                 | 11.8        |
| Trp(W)     | 14.5 ± 0.2              | 11.5                 | 15.0        |
| His(H)     | 18.0 ± 1.0              | 13.3                 | 23.1        |
| Lys(K)     | 19.8 ± 1.2              | >13.3                | 23.6        |
| Arg(R)     | >26.8                   | >13.3                | 36.9        |

[a] $\Delta G^\circ_{Ag} \approx \Delta H^\circ_{Ag}$ except for His, Lys and Arg; uncertainties show standard deviations of 5 measurements; $T_{eff} = 902 \pm 26$ K.

**Fluorescence Quenching Mechanism**

In order to investigate the mechanism of the metal-ion induced fluorescence quenching of CDs, the fluorescence lifetime (FL) of the CDs was monitored before and after adding Cu(II) (Fig. 6). The fluorescence decay curves of three CDs can be fitted by a single-exponential formula respectively with a similar lifetime ($FL_{G-CD} = 3.2567$ ns; $FL_{L-CD} = 3.4580$; $FL_{H-CD} = 2.8621$). The FL of the CDs almost stayed unchanged in the presence of Cu(II), indicating a time-independant mechanism. Therefore, a static quenching mechanism could account for the response behavior of the CDs to Cu(II) [41, 42]. A
nonfluorescent ground-state complex should be formed between the CDs and metal ions, which immediately returns to the ground-state without emission of a photon after absorbing light.

**Conclusions**

In summary, we prepared three kinds of CDs through adopting specific carbon source in order to predetermine their ion-sensing capability. The carbon source, including glycine, histidine and leucine, has been confirmed to bind with Cu(II) and Ag(I). The as-prepared CDs inherited the binding capability from their corresponding carbon source. The binded metal ions quenched the fluorescence of the CDs through a static mechanism, based on which quantitative determination of Cu(II) and Ag(I) can be realized. Moreover, there existed an inherent relationship between the ion-determining capability of the CDs and the binding energy between their corresponding carbon source and metal ions. These results provided valuable reference value for the design of the sensors based on CDs.

**Declarations**

**Data Availability**

The data used to support the findings of this study are included within the article.

**Authors’ Contributions**

All authors contributed to the study conception and design. Manling Chen: Investigation, Writing - Original Draft, Reviewing and Editing; Xue Liu: Conceptualization, Supervision, Project administration, Funding acquisition, Reviewing and Editing.

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**Compliance with Ethical Standards**

**Competing Interests**

The authors have no relevant financial or non-financial interests to disclose.

**Code Availability**

Not applicable.
References

1. Baker SN, Baker GA (2010) Luminescent Carbon Nanodots: Emergent Nanolights. Angew Chem Int Ed 49 (38):6726-6744. doi:10.1002/anie.200906623

2. Li H, Kang Z, Liu Y, Lee S-T (2012) Carbon nanodots: synthesis, properties and applications. J Mater Chem 22 (46):24320-24253. doi:10.1039/C2JM34690G

3. Lim SY, Shen W, Gao Z (2015) Carbon quantum dots and their applications. Chem Soc Rev 44 (1):362-381. doi:10.1039/C4CS00269E

4. Wu Y, Liu X, Wu Q, Yi J, Zhang G (2017) Differentiation and determination of metal ions using fluorescent sensor array based on carbon nanodots. Sens Actuators B Chem 246:680-685. doi:https://doi.org/10.1016/j.snb.2017.02.132

5. Zhang K, Zhou H, Mei Q, Wang S, Guan G, Liu R, Zhang J, Zhang Z (2011) Instant Visual Detection of Trinitrotoluene Particulates on Various Surfaces by Ratiometric Fluorescence of Dual-Emission Quantum Dots Hybrid. J Am Chem Soc 133 (22):8424-8427. doi:10.1021/ja2015873

6. Wu Y, Liu X, Wu Q, Yi J, Zhang G (2017) Carbon Nanodots-Based Fluorescent Turn-On Sensor Array for Biothiols. Anal Chem 89 (13):7084-7089. doi:10.1021/acs.analchem.7b00956

7. Guo Y, Zhang L, Zhang S, Yang Y, Chen X, Zhang M (2015) Fluorescent carbon nanoparticles for the fluorescent detection of metal ions. Biosens Bioelectron 63:61-71. doi:https://doi.org/10.1016/j.bios.2014.07.018

8. Zheng M, Xie Z, Qu D, Li D, Du P, Jing X, Sun Z (2013) On–Off–On Fluorescent Carbon Dot Nanosensor for Recognition of Chromium(VI) and Ascorbic Acid Based on the Inner Filter Effect. ACS Appl Mater Interfaces 5 (24):13242-13247. doi:10.1021/am4042355

9. Sun X, Lei Y (2017) Fluorescent carbon dots and their sensing applications. Trends Analyt Chem 89:163-180. doi:https://doi.org/10.1016/j.trac.2017.02.001

10. Liu S, Tian J, Wang L, Zhang Y, Qin X, Luo Y, Asiri AM, Al-Youbi AO, Sun X (2012) Hydrothermal treatment of grass: a low-cost, green route to nitrogen-doped, carbon-rich, photoluminescent polymer nanodots as an effective fluorescent sensing platform for label-free detection of Cu(II) ions. Adv Mater 24 (15):2037-2041. doi:10.1002/adma.201200164

11. Yuan C, Liu B, Liu F, Han MY, Zhang Z (2014) Fluorescence “turn on” detection of mercuric ion based on bis(dithiocarbamato)copper(II) complex functionalized carbon nanodots. Anal Chem 86 (2):1123-1130. doi:10.1021/ac402894z

12. Castro JL, López Ramírez MR, López Tocón I, Otero JC (2003) Vibrational study of the metal–adsorbate interaction of phenylacetic acid and α-phenylglycine on silver surfaces. J Colloid Interface Sci 263 (2):357-363. doi:10.1016/s0021-9797(03)00257-1

13. Lee VWM, Li H, Lau T-C, Guevremont R, Michael Siu KW (1998) Relative silver(I) ion binding energies of α-amino acids: A determination by means of the kinetic method. J Am Soc Mass Spectrom 9 (8):760-766. doi:10.1016/S1044-0305(98)00051-8
14. Nimse S, Pal D (2015) Free Radicals, Natural Antioxidants, and their Reaction Mechanisms. RSC Adv 5:27986-28006. doi:10.1039/C4RA13315C
15. Thomas G, Zacharias PS (1985) Mixed ligand Cu(II) amino acid complexes containing 2,2'-bipyridyl. Cyclic voltammetric studies of the reduction in aqueous media. Polyhedron 4 (2):299-301. doi:https://doi.org/10.1016/S0277-5387(00)84502-7
16. Choi S-H, Lee S-H, Hwang Y-M, Lee K-P, Kang H-D (2003) Interaction between the surface of the silver nanoparticles prepared by γ-irradiation and organic molecules containing thiol group. Radiat Phys Chem 67 (3):517-521. doi:https://doi.org/10.1016/S0969-806X(03)00097-5
17. Ye R, Xiang C, Lin J, Peng Z, Huang K, Yan Z, Cook N, Samuel E, Hwang C-C, Ruan G, Ceriotti G, Raji A-R, Martí A, Tour J (2013) Corrigendum: Coal as an abundant source of graphene quantum dots. Nat commun 4:2943-2948. doi:10.1039/ncomms3943
18. Zhu S, Song Y, Wang J, Wan H, Zhang Y, Ning Y, Yang B (2017) Photoluminescence mechanism in graphene quantum dots: Quantum confinement effect and surface/edge state. Nano Today 13:10-14. doi:https://doi.org/10.1016/j.nantod.2016.12.006
19. Ju J, Zhang R, He S, Chen W (2014) Nitrogen-doped graphene quantum dots-based fluorescent probe for the sensitive turn-on detection of glutathione and its cellular imaging. RSC Adv 4 (94):52583-52589. doi:10.1039/C4RA10601F
20. Zhu S, Meng Q, Wang L, Zhang J, Song Y, Jin H, Zhang K, Sun H, Wang H, Yang B (2013) Highly Photoluminescent Carbon Dots for Multicolor Patterning, Sensors, and Bioimaging. Angew Chem Int Ed 52 (14):3953-3957. doi:10.1002/anie.201300519
21. Shen C, Sun Y, Wang J, Lu Y (2014) Facile route to highly photoluminescent carbon nanodots for ion detection, pH sensors and bioimaging. Nanoscale 6 (15):9139-9147. doi:10.1039/C4NR02154A
22. Wang D, Wang L, Dong X, Shi Z, Jin J (2012) Chemically tailoring graphene oxides into fluorescent nanosheets for Fe$^{3+}$ ion detection. Carbon 50 (6):2147-2154. doi:https://doi.org/10.1016/j.carbon.2012.01.021
23. Zhu S, Song Y, Zhao X, Shao J, Zhang J, Yang B (2015) The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. Nano Res 8 (2):355-381. doi:10.1007/s12274-014-0644-3
24. Sun X, He J, Meng Y, Zhang L, Zhang S, Ma X, Dey S, Zhao J, Lei Y (2016) Microwave-assisted ultrafast and facile synthesis of fluorescent carbon nanoparticles from a single precursor: preparation, characterization and their application for the highly selective detection of explosive picric acid. J Mater Chem A 4 (11):4161-4171. doi:10.1039/C5TA10027E
25. Song Y, Zhu S, Zhang S, Fu Y, Wang L, Zhao X, Yang B (2015) Investigation from chemical structure to photoluminescent mechanism: a type of carbon dots from the pyrolysis of citric acid and an amine. J Mater Chem C 3 (23):5976-5984. doi:10.1039/C5TC00813A
26. Ananthanarayanan A, Wang X, Routh P, Sana B, Lim S, Kim DH, Lim K, Li J, Chen P (2014) Facile Synthesis of Graphene Quantum Dots from 3D Graphene and their Application for Fe$^{3+}$ Sensing. Adv Funct Mater 24 (20):3021-3026. doi:10.1002/adfm.201303441
27. Chandra S, Laha D, Pramanik A, Ray Chowdhuri A, Karmakar P, Sahu SK (2016) Synthesis of highly fluorescent nitrogen and phosphorus doped carbon dots for the detection of Fe(3+) ions in cancer cells. Luminescence 31 (1):81-87. doi:10.1002/bio.2927

28. Huang Y, Zhou J, Feng H, Zheng J, Ma H-M, Liu W, Tang C, Ao H, Zhao M, Qian Z (2016) A dual-channel fluorescent chemosensor for discriminative detection of glutathione based on functionalized carbon quantum dots. Biosens Bioelectron 86:748-755. doi:https://doi.org/10.1016/j.bios.2016.07.081

29. Song Z, Quan F, Xu Y, Liu M, Cui L, Liu J (2016) Multifunctional N,S co-doped carbon quantum dots with pH- and thermo-dependent switchable fluorescent properties and highly selective detection of glutathione. Carbon 104:169-178. doi:https://doi.org/10.1016/j.carbon.2016.04.003

30. Gao X, Du C, Zhuang Z, Chen W (2016) Carbon quantum dot-based nanoprobes for metal ion detection. J Mater Chem C 4 (29):6927-6945. doi:10.1039/C6TC02055K

31. Chen J, Li Y, Lv K, Zhong W, Wang H, Wu Z, Yi P, Jiang J (2016) Cyclam-functionalized carbon dots sensor for sensitive and selective detection of copper(II) ion and sulfide anion in aqueous media and its imaging in live cells. Sens Actuators B Chem 224:298-306. doi:https://doi.org/10.1016/j.snb.2015.10.046

32. Martin R-P, Mosoni L, Sarkar B (1971) Ternary Coordination Complexes between Glycine, Copper (II), and Glycine Peptides in Aqueous Solution. J Biol Chem 246 (19):5944-5951. doi:https://doi.org/10.1016/S0021-9258(18)61818-6

33. Nyberg M, Odelius M, Nilsson A, Pettersson L (2003) Hydrogen bonding between adsorbed deprotonated glycine molecules on Cu(110). J Chem Phys 119:12577-12585. doi:10.1063/1.1625640

34. Caraiman D, Shoeib T, Michael Siu KW, Hopkinson AC, Bohme DK (2003) Investigations of the gas-phase reactivity of Cu+ and Ag+ glycine complexes towards CO, D2O and NH3. Int J Mass Spectrom 228 (2):629-646. doi:https://doi.org/10.1016/S1387-3806(03)00210-0

35. Nomiya K, Takahashi S, Noguchi R, Nemoto S, Takayama T, Oda M (2000) Synthesis and Characterization of Water-Soluble Silver(I) Complexes with l-Histidine (H2his) and (S)-(−)-2-Pyrrolidone-5-carboxylic Acid (H2pyrrld) Showing a Wide Spectrum of Effective Antibacterial and Antifungal Activities. Crystal Structures of Chiral Helical Polymers [Ag(Hhis)]n and {[Ag(Hpyrrld)]2}n in the Solid State. Inorg Chem 39 (15):3301-3311. doi:10.1021/ic990526o

36. Abbaspour A, Kamyabi MA (2004) Characterization and determination of stability constants of copper(II)–l-histidine complexation system by using multivariate curve resolution method of visible spectra and two hard modeling methods in aqueous solutions. Anal Chim Acta 512 (2):257-269. doi:https://doi.org/10.1016/j.aca.2004.02.056

37. Inci D, Aydin R, Zorlu Y (2016) Affinity of a new copper(II) complex to DNA/BSA and antioxidant/ radical scavenging activities: crystal structure of [Cu(4,7-diphenyl-1,10-phenanthroline) (leucine)(NO3)(H2O)]. J Coord Chem 69 (18):2677-2696. doi:10.1080/00958972.2016.1213390
38. Gatlin CL, Tureček F, Vaisar T (1995) Gas-phase complexes of amino acids with Cu(II) and diimine ligands. Part I. Aliphatic and aromatic amino acids. J Mass Spectrom 30 (11):1605-1616. doi:10.1002/jms.1190301114

39. Gatlin CL, Tureček F, Vaisar T (1995) Gas-phase complexes of amino acids with Cu(II) and diimine ligands. Part II. Amino acids with O, N and S functional groups in the side-chain. J Mass Spectrom 30 (11):1617-1627. doi:10.1002/jms.1190301115

40. Shoeib T, Siu KWM, Hopkinson AC (2002) Silver Ion Binding Energies of Amino Acids: Use of Theory to Assess the Validity of Experimental Silver Ion Basicities Obtained from the Kinetic Method. J Phys Chem A 106 (25):6121-6128. doi:10.1021/jp013662z

41. Liu X, Li T, Wu Q, Yan X, Wu C, Chen X, Zhang G (2017) Carbon nanodots as a fluorescence sensor for rapid and sensitive detection of Cr(VI) and their multifunctional applications. Talanta 165:216-222. doi:https://doi.org/10.1016/j.talanta.2016.12.037

42. Hou Y, Liu X, Tang X, Li T, Wu Q, Jiang Y, Yi J, Zhang G (2017) Nucleobase chemosensor based on carbon nanodots. Talanta 173:107-112. doi:https://doi.org/10.1016/j.talanta.2017.05.071