Fluorescent and electrochemical detection of Cu (II) ions in aqueous environment by a novel, simple and readily available AIE probe

Erman Karakuş (Conceptualization) (Methodology) (Formal analysis) (Writing - original draft) (Writing - review and editing), Simay Gunduz (Conceptualization) (Formal analysis) (Investigation), Lokman Liv (Methodology) (Formal analysis) (Writing - original draft), Turan Ozturk (Investigation) (Supervision)

PII: S1010-6030(20)30501-3

DOI: https://doi.org/10.1016/j.jphotochem.2020.112702

Reference: JPC 112702

To appear in: *Journal of Photochemistry & Photobiology, A: Chemistry*

Received Date: 13 January 2020

Revised Date: 9 June 2020

Accepted Date: 10 June 2020

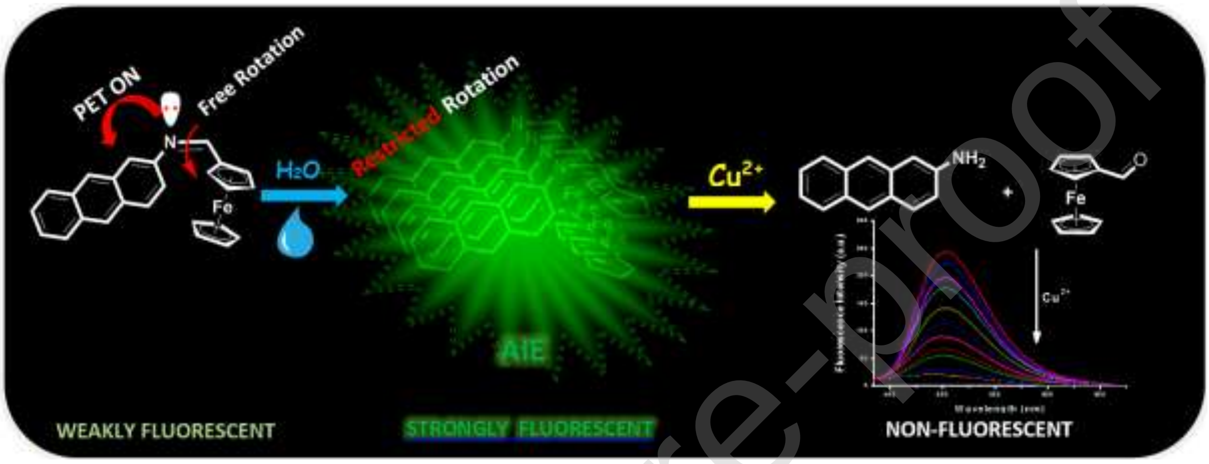
Please cite this article as: { doi: https://doi.org/

Fluorescent and Electrochemical Detection of Cu (II) ions in Aqueous Environment by a Novel, Simple and Readily Available AIE Probe

Erman Karakuş*[a], Simay Gunduz[a], Lokman Liv[b] and Turan Ozturk[a,c]

[a]Organic Chemistry Laboratory, Chemistry Group, National Metrology Institute, (TUBITAK UME), 41470 Gebze, Kocaeli, Turkey erman.karakus@tubitak.gov.tr
[b]Electrochemistry Laboratory, Chemistry Group, National Metrology Institute, (TUBITAK UME), 41470, Gebze, Kocaeli, Turkey
[c] Istanbul Technical University, Department of Chemistry, 34469 Maslak, Istanbul, Turkey

Graphical abstract



Highlights

- An anthracene molecule incorporated with ferrocene group was designed for the selective and sensitive detection of Cu^{2+} ions in aqueous media.
- The probe (**ANT-Fe**) is synthesized so easily by mixing commercially available two reactants without needed column chromatography for the purification process.
- **ANT-Fe** exhibited dual sensing, both fluorometric “turn-off” and electrochemical signaling mode with a cathodic shift, for the detection of Cu^{2+} ions (LOD = 2.5 ppb) in aqueous media.
- **ANT-Fe** also showed aggregation induced emission (AIE) property.
- Detection of Cu^{2+} ions with **ANT-Fe** adsorbed on the test paper system was successfully achieved as a practical application.

ABSTRACT

We have devised a novel and fluorescent chemodosimeter (**ANT-Fe)**, possessing an anthracene scaffold as a fluorophore and ferrocene as a redox active unit for selective and sensitive detection of Cu^{2+} ions in aqueous media. Its synthesis was realized by a simple combination of two commercially available compounds, 2-aminoanthracene and ferrocenecarboxaldehyde, in one-step without required column chromatography for the purification process. The probe offers distinct properties such as aggregation induced emission, dual sensing mode of fluorometric “turn-off” and electrochemical signaling with cathodic shift, high selectivity towards Cu^{2+} ions, fast response time and low detection limit (2.5 ppb) *via* C=N bond hydrolysis. Detection of Cu^{2+} ions by **ANT-Fe** adsorbed on a test paper system with the naked eye as a practical application is also successfully reported.

Keywords: Anthracene, Ferrocene, Aggregation-induced-emission, Copper (II) probe, Fluorometric sensor, Electrochemical sensor.

1. Introduction

The design of fluorescent molecular sensors for the detection of transition and heavy metal species has received a great deal of attention. Since these species not only play significant roles in various biological processes but also have extremely toxic effect on the environment[1–5]. Copper ion is the third most abundant metal ion (after iron and zinc) in the human body and plays an essential role in various environmental, chemical and biological systems [6–10]. For example, copper ion serves as a catalytic co-factor for a different type of metalloenzymes including superoxide dismutase, cytochrome oxidase and tyrosinase [11–13]. However, in sharp contrast to its beneficial effects, misregulation or abnormal accumulation of copper ion may cause several diseases such as Alzheimer's and Parkinson's diseases [14,15]. The normal level of total copper in the blood sample is the range from 15.7 to 23.6 μM and the U.S. Environmental Protection Agency (EPA) has set a limit for copper ion in drinking water of 20.0 μM [16]. Therefore, constructing and developing selective and sensitive signalling frameworks for determining copper ion warrants research for improved chemo-sensing and molecular imaging.

In recent years, different types of fluorophores such as BODIPY, rhodamine, fluorescein, coumarin and anthracene have been used for the detection of copper ions in various emerging fields [3,16–19]. The fluorometric methods have many preferable advantages for instance simplicity, fast response, low cost, high sensitivity and reproducibility concerning the traditional techniques such as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and inductively coupled plasma mass spectroscopy (ICP-MS). While some organic molecules, bearing π-conjugated chromophores, display aggregation caused quenching (ACQ) property, which may limit their use in practical applications [20], some molecules possess aggregation induced emission (AIE) phenomena [21]. Fluorescent molecules having AIE property exhibit poor emission in organic solutions but emit high radiation in their aggregate form. Such molecules can be used as biosensors, organic light emitting diodes (OLEDs) and fluorescent probes [22]. Fluorescent probes with AIE for the detection of metal ions are now available in the literature [23–30]. The main advantage of AIE probes is that they mostly work in aqueous medium and water provides aggregation leading to intensity increment causing a low detection limit. However, AIE probes have some disadvantages such as synthetic difficulties, high cost and poor limit of detection. Therefore, the design and synthesis of molecules with low cost and a better detection limit is a challenge.

Anthracene, as an AIE fluorophore has attracted our attention due to its simple structure, chemical stability and easy to modify [26, 28–30]. Moreover, ferrocene with its unique electrochemical property and high stability appears to be a suitable reactive unit for designing fluorescent probes [31–36]. In this regard, we envisaged that incorporating both an AIE fluorophore and electrochemically active unit into a single structure could provide an efficient sensing platform for the detection of copper (II) ions for dual signalling response. To the best of our knowledge, molecular sensors displaying three different features i.e. AIE, electrochemical activity and fluorescence for the detection of copper ions have not been covered in the literature.

Thus, herein, we report an easy one-step synthesis of a novel Schiff base probe bearing 2-aminoanthracene (AIE fluorophore) and ferrocenecarboxaldehyde (electrochemically active molecule) to detect copper ions in aqueous media. We have concentrated on utilizing the new AIE host molecule modified with redox active ferrocene unit, which provides a well-flexible and extensively conjugated ligand system to interact with guest copper ions. The obtained probe, due to water-insolubility nature (forming aggregates), exhibits strong green emission and irreversible electrode reaction. When interacting with copper (II) ions, the probe demonstrates “turn off” sensing event with irreversible chemical and reversible electrode reactions with cathodic potential shift. Besides, fluorescent test papers were applied for instant “naked eye” detection of copper (II) ions.

2. Experimental Details

2.1. General Methods

All reagents were purchased from commercial suppliers (Aldrich and Merck) and used without further purification. ^{1}H NMR and ^{13}C NMR were measured on a Varian VNMRJ 600 Nuclear Magnetic Resonance Spectrometer. Mass analysis was conducted with Thermo Q Exactive Orbitrap device. Fluorescence emission spectra were obtained using Varian Cary Eclipse Fluorescence spectrophotometer. Quantum yield measurements were conducted with Hamamatsu Quantaurus-QY Absolute PL quantum yield spectrometer. Particle size distribution analysis was determined by dynamic light scattering (DLS) method with Malvern Mastersizer 2000 instrument. The electrochemical measurements were performed by Metrohm Autolab PGSTAT 128N potentiostat/galvanostat instrument and BASi C3 voltammetric cell stand under an argon atmosphere at 21 ± 3 °C. The quartz voltammetric cell was used for electrochemical measurements.

2.2. Preparation of UV-vis and Emission Measurement Solutions

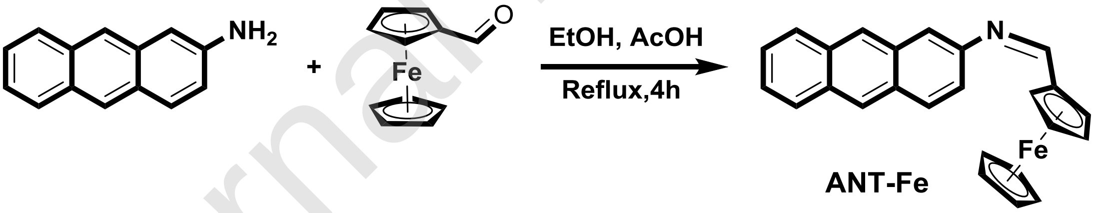
The stock solution of probe molecule **ANT-Fe** (1 mM) was prepared in CH_3CN and stock solutions of metal ion salts (20 mM) were prepared in triple distilled deionized water. During the measurements, the metal ion solution was added into the probe solution (2 mL) using a micropipette. For fluorescence measurements, samples were contained in 10.0 mm path length quartz cuvettes (2.0 mL volume). Upon excitation at 400 nm, the emission spectra were integrated over the range 410 nm to 700 nm (Both excitation and emission slit width 5 nm / 5 nm). All measurements were conducted in triplicate at least.

2.3. Electrochemical Experiments

Three electrode system consisting of glassy carbon (BASi MF-2012, 3.0 mm dia.) as a working electrode (GCE), Ag/AgCl (sat. NaCl) (BASi MF-2052) as a reference electrode and Pt wire (BASi MW-1032) as an auxiliary electrode was used. GCE surface was polished with 0.05 µm Al_2O_3-water and Al_2O_3-ethanol slurry on synthetic cloth, washed with deionized water and ethanol a couple of times, respectively. Afterward, it was ultrasonicated in 1:1 ethanol: deionized water and deionized water by turns. Differential pulse voltammetry (DPV) measurements were performed with 5 mV step potential, 25 mV pulse amplitude, 50 ms pulse width and 0.5 s interval time, respectively. Cyclic voltammetry (CV) measurements were performed with 2.5 mV step potential and 0.1 V/s scan rate by turns. The concentration of **ANT-Fe** for DPV/CV experiments is 200 μM in 4:1 CH_3CN : HEPES (v/v) solution at pH = 7.0.

2.4. Synthesis of **ANT-Fe**

2-aminoanthracene (0.15 g, 0.78 mmol) and ferrocenecarboxaldehyde (0.17 g, 0.78 mmol) were mixed in 15 mL ethanol in the presence of catalytic amount (2-3 drops) acetic acid. The solution mixture was refluxed for 4h under nitrogen atmosphere. The obtained solid was filtered and recrystallized in an EtOH-CH_2Cl_2 mixture (3:1 v/v) to get desired product **ANT-Fe** as a white solid (80 %). ^{1}H-NMR (600 MHz, d-DMSO): δ ppm 8.60 (s, 1H), 8.54 (d, J = 11.7 Hz, 2H), 8.08 – 8.02 (m, 3H), 7.72 (s, 1H), 7.49 – 7.44 (m, 3H), 4.85 (s, 2H), 4.56 (s, 2H), 4.30 (s, 5H). APT ^{13}C-NMR (150 MHz, d-DMSO): δ ppm 164.6, 152.6, 135.2, 134.7, 133.8, 132.8, 132.3, 131.3, 131.0, 129.1, 128.9, 128.7, 128.3, 125.3, 119.1, 83.7, 74.4, 72.3, 72.1. HRMS: m/z: Calcd. for ($C_{25}H_{19}FeN$) [M+H$^+$]: 390.09397; found, 390.09338.



Scheme 1: Synthesis pathway of **ANT-Fe**

3. Results and Discussion

The probe molecule **ANT-Fe** was prepared *via* easy one-step acid catalyzed Schiff-base condensation reaction of commercially available 2-aminoanthracene and ferrocenecarboxaldehyde in good yield (80 %) (Scheme 1). The structure of the probe was unambiguously confirmed by ^{1}H NMR, ^{13}C NMR and HRMS techniques, as detailed in the Supporting Information (SI).

The aggregation induced emission (AIE) behavior in response to different ratios of several organic-aqueous solvent mixtures was investigated by using UV-visible and fluorescence spectroscopy. We commenced our investigation by examining the solution media. Solvatochromism experiment was performed in different polar solvents (Fig S1). After various solvent combinations such as DMSO-H_2O, EtOH-H_2O and CH_3CN-H_2O, a mixture of CH_3CN-H_2O was found to be a highly efficient system in which **ANT-Fe** displayed two adsorption bands at 262 and 350 nm. An increase in water content resulted in a gradual decline in the absorbance and absorbance reached its minimum at 70 % water, after which insoluble particles started to appear in solution (Fig S2). Concerning the fluorescence, the opposite trend was observed (Figure 1). In CH_3CN solution, **ANT-Fe** (10 µM) displayed a poor emission intensity at 490 nm when excited at 400 nm. On the other hand, the fluorescence intensity enhanced with the increase in water content (up to 70 % level) along with a shift at fluorescence maxima from 490 nm to 502 nm. Such shift was explained to be due to the H- and J-type aggregates causing blue and red-shifts, respectively [26]. Mechanism of this phenomenon, as well defined in the literature, AIE, resembles in many aspects of the previously published works [26,30,37–39]. The restriction of intramolecular rotation (RIR) through the addition of water induces AIE property as the single bond rotation mostly responsible for non-radiative decay in the solution [40]. While maximum AIE fluorescence intensity was reached at %70 of water content ($\Phi_F = 0.44$), the addition of more water gave rise to a decrease in the emission intensity (Figure 1). This could be explained that as the solvating ability of aqueous mixture decreases with increasing water content, the formation of proper crystals was prevented with the formation of amorphous aggregates of smaller sizes [23]. AIE property of **ANT-Fe** was also supported by particle size distribution analysis, i.e. DLS method, which exhibited the sizes of aggregates acquired in CH_3CN-H_2O mixtures of 40% and 70% to be 207 nm and 667 nm mean diameters respectively. When the amount of water was increased to 90% ($\Phi_F = 0.22$) the size of aggregates declined to 376 nm similar to the reports released earlier [26,39].

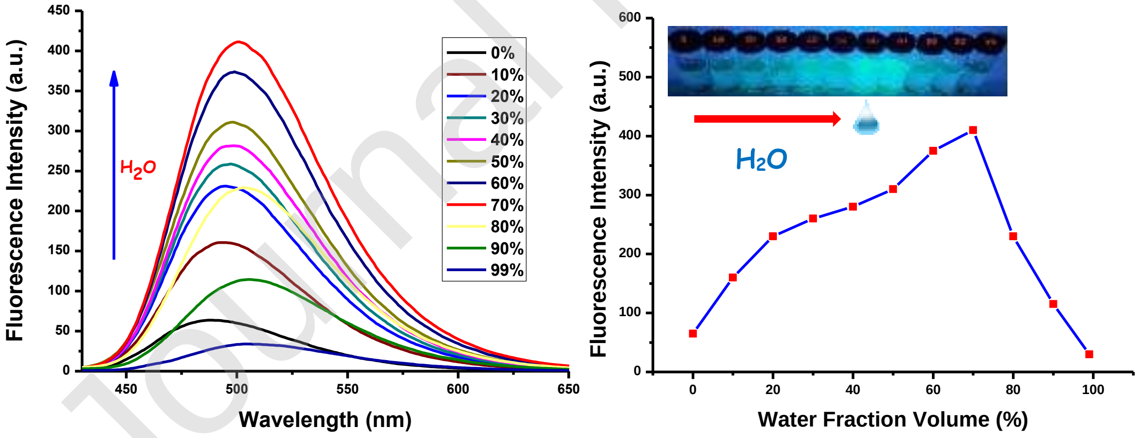


Fig. 1. Fluorescence intensity change spectrum of **ANT-Fe** (10 µM) in CH_3CN with increasing volume of water percentages from 0% to 99%.

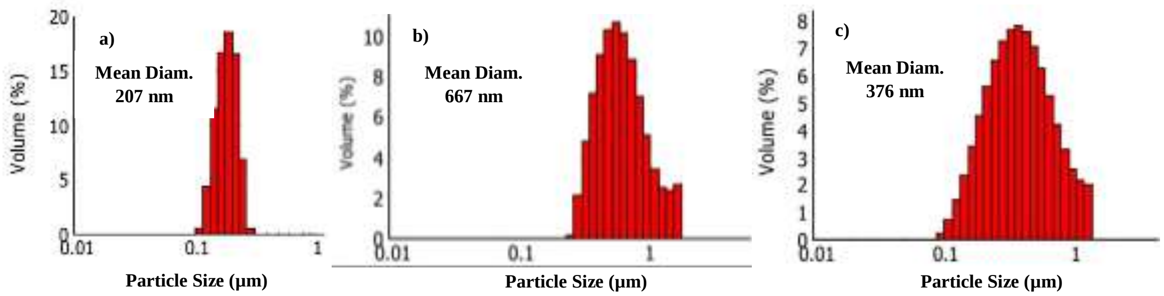


Fig. 2. The particle size distribution of **ANT-Fe** (10 µM) in mixed aqueous solutions (CH_3CN/H_2O) of (a) 40%, (b) 70% and (c) 90% volume of water content determined by DLS measurements

After investigation AIE property, we mainly focused on the chemical sensing ability of the **ANT-Fe** towards copper (II) ions (Cu^{2+}). The spectral properties of the probe were examined under simulated physiological conditions HEPES buffer (10 mM) - CH_3CN (pH=7.0, v/v 4:1). Also, the possible effects of pH changes in the detection of Cu^{2+} ions were investigated. Remarkably, the **ANT-Fe** was affected slightly by pH fluctuations (pH 2.0 – 9.0) on the fluorescence intensity of the sensing media (Fig S3). Free **ANT-Fe** (HEPES/CH_3CN 4:1, pH= 7.0) showed a maximum fluorescence emission band at 505 nm upon excitation at 400 nm, belonging to the anthracene fluorophore (Figure 3), which could be attributed to aggregation induced emission discussed above. As anticipated, the fluorescence intensity dramatically decreased by the addition of different concentrations of Cu^{2+} ions. **ANT-Fe** displayed "turn-off" response in 15 s and the decline of the emission intensity (>20 fold) became saturated within 5 min (Fig S4). Detection limit of **ANT-Fe** was determined as 2.5 ppb (40 nM) based on signal-to-noise ratio (S/N = 3) (Fig S5).

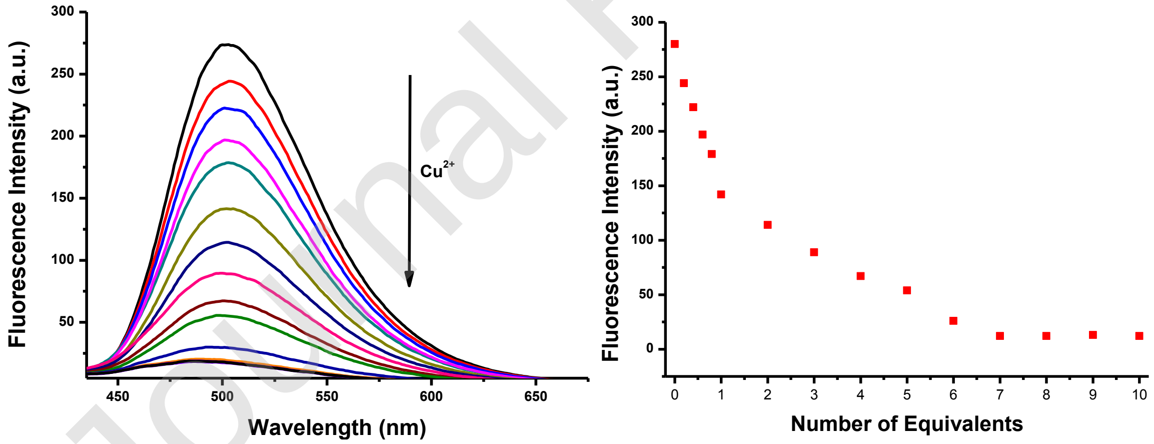


Fig. 3. Emission titration curve of **ANT-Fe** (10 µM) and Cu^{2+} (0-10 equiv.) in 4:1 HEPES/CH_3CN at pH = 7.0 (λ_{ex} : 400 nm)

The selectivity study of **ANT-Fe** to other possible metal ions, including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+} was investigated under the same sensing situation. All other metal species except for Cu^{2+} did not cause any spectral change, fortunately (Figure

4a). Also, it was examined the possible interference of other metal ions via competitive experiment and the **ANT-Fe** easily detected Cu^{2+} in the mixtures of other related species (Figure 4b).

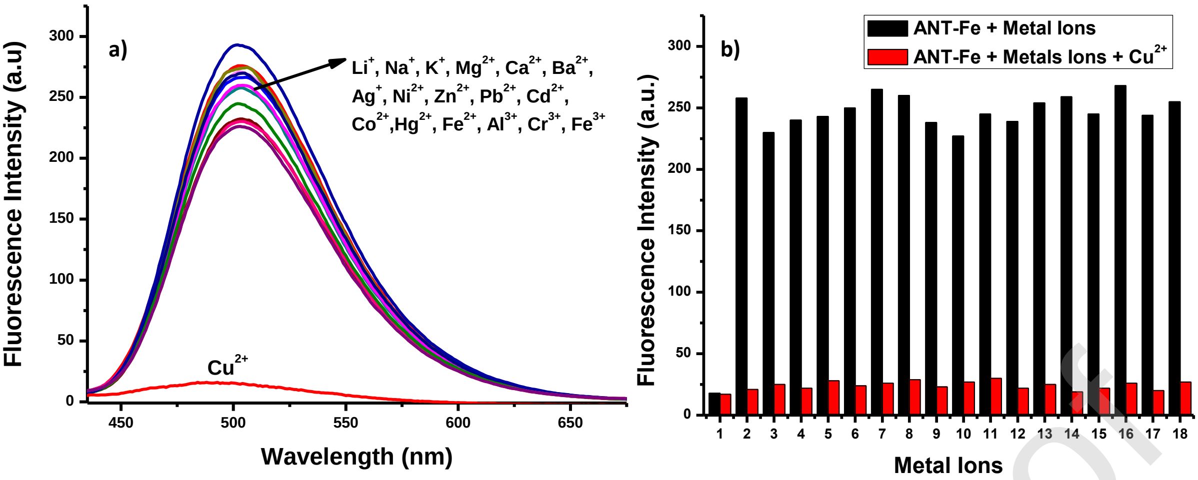
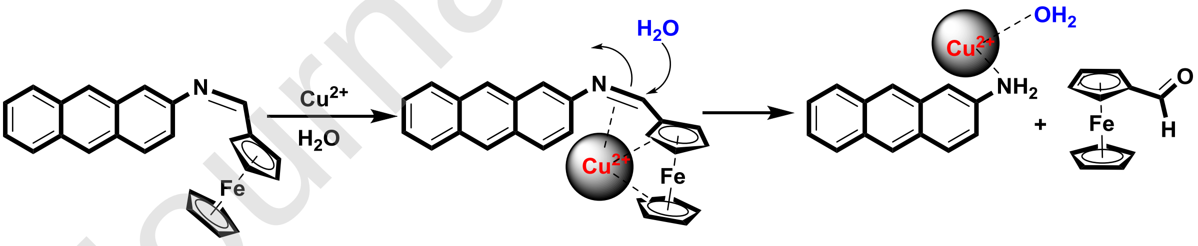


Fig. 4. (a) Fluorescence intensities of **ANT-Fe** (10 μM) in 4:1 HEPES/CH_3CN at pH = 7.0 in the presence of Cu^{2+} (5.0 equiv) and other metal ions (10.0 equiv). (b) Fluorescence intensities of **ANT-Fe** (10 μM) in 4:1 HEPES/CH_3CN at pH = 7.0 in the presence of Cu^{2+} (5.0 equiv) and 50.0 equiv other metal ions 1, Cu^{2+}; 2, Li^{+}; 3, Na^{+}; 4, K^{+}; 5, Mg^{2+}; 6, Ca^{2+}; 7, Ba^{2+}; 8, Ag^{+}; 9, Ni^{2+}; 10, Zn^{2+}; 11, Pb^{2+}; 12, Cd^{2+}; 13, Co^{2+}; 14, Hg^{2+}; 15, Fe^{2+}; 16, Al^{3+}; 17, Cr^{3+}; 18, Fe^{3+}

To understand the nature of the overall sensing process to be irreversible or not, an excess amount of CN^{-}, $S^{2-}$and cysteine (10.0 equiv.) were subjected to **ANT-Fe** solution containing Cu^{2+} ions. Any spectral change was not observed, which verified the irreversibility of the sensing mechanism. The sensing mechanism was proposed to proceed through the simultaneous coordination of Cu^{2+} ions with nitrogen atom on C=N moiety by the aid of the electron donor character of ferrocene molecule. This coordination somehow promoted rapid hydrolysis of C=N bond *via* an attack of water to imine moiety, causing formation of 2-aminoanthracene copper complex and ferrocenecarboxaldehyde.



Scheme 2. Proposed mechanism for the detection of Cu^{2+} ions

NMR analysis was used to support the proposed sensing mechanism. The NMR data indicated that, upon treatment of **ANT-Fe** solution with Cu^{2+} ions, the imine proton signal at 8.60 ppm disappeared and a new aldehyde proton, belonging ferrocenecarboxyaldehyde, formed at 9.87 ppm. This result proved that Cu^{2+} ion mediated hydrolysis reaction took place.

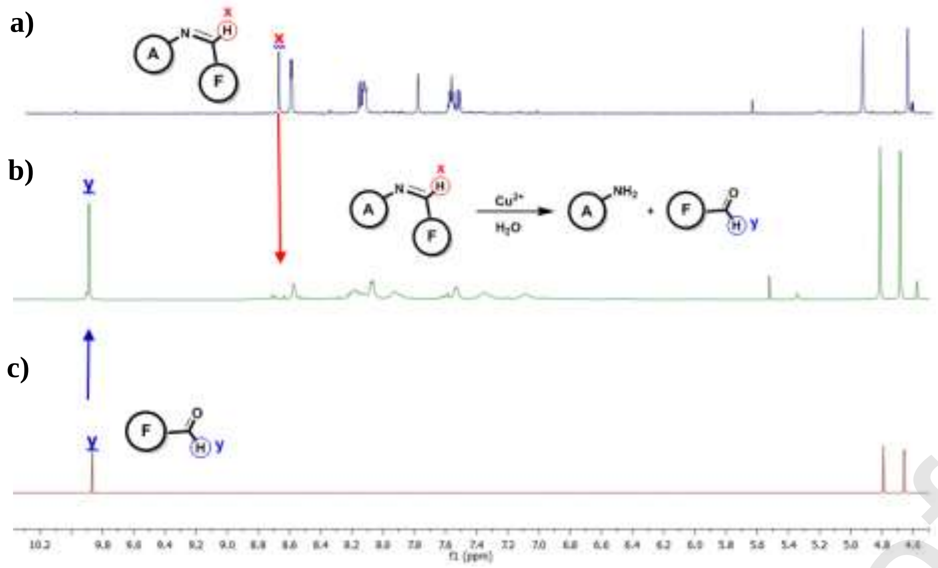


Fig. 5. (a) Partial ^{1}H NMR spectra of **ANT-Fe**, (b) **ANT-Fe** + 1 eq. Cu^{2+} (c) ferrocenecarboxaldehyde

Since the probe **ANT-Fe** consists of two redox active sites, i.e. ferrocene and imine, it would worth studying electrochemistry of the interaction of **ANT-Fe** with Cu^{2+} ions. Therefore, electrochemical behaviours of **ANT-Fe** and Cu^{2+} were investigated by using CV and DPV techniques. The probe demonstrated an irreversible electrode reaction at 615 mV belonging to electron donating ferrocene part. However, the addition of Cu^{2+} induced a reversible electrode reaction with a cathodic potential shift of 50 mV due to the formation of ferrocenecarboxaldehyde through the hydrolysis reaction between **ANT-Fe** and Cu^{2+}. This result is also consistent with pure ferrocenecarboxaldehyde electrochemical signal under the same condition which is another evidence of the hydrolysis reaction (Figure 6).

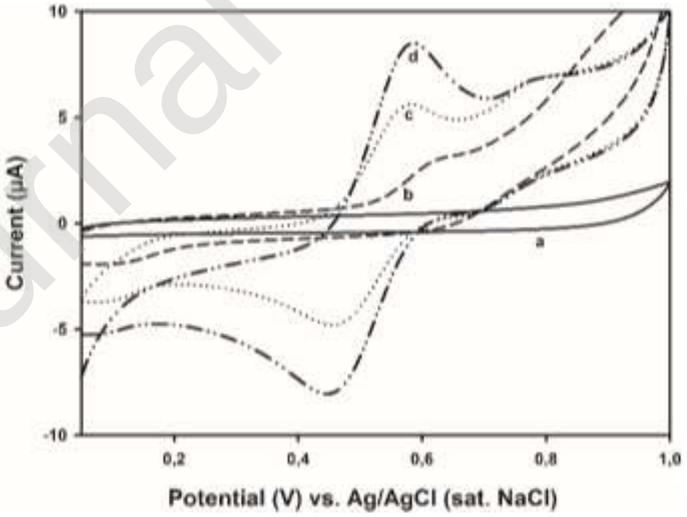


Fig. 6. CVs results of **(a)** acetonitrile, **(b)** 200 µM **ANT-Fe** only **(c) ANT-Fe** and 2.5 equivalent Cu^{2+} **(d)** pure ferrocenecarboxaldehyde only (in 4:1 CH_3CN : HEPES (v/v) solution at pH = 7.0)

CV and DPV titrations of **ANT-Fe** with different amount of Cu^{2+} are depicted in Figure 7. Cu^{2+} addition resulted in a cathodic potential shift due to the formation electrochemically active ferrocenecarboxaldehyde which could be attributed different chemical nature of bounded and unbounded ferrocenecarboxaldehyde. The **ANT-Fe** became completely saturated with the addition of 9 equivalents of Cu^{2+}.

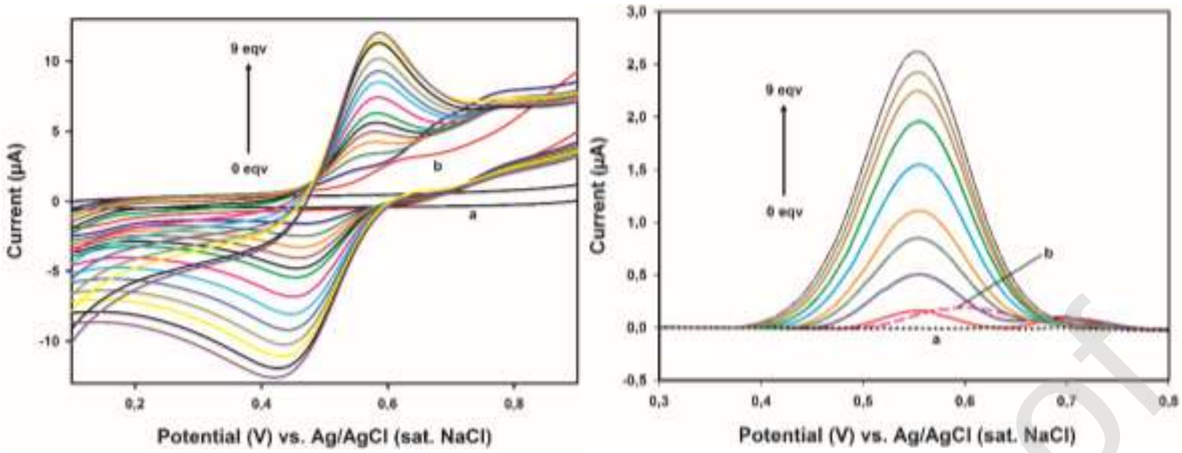


Fig. 7. CV and DPV titrations of the **ANT-Fe** with addition of different concentrations of Cu^{2+} (0 – 9 equiv.) **(a)**: Acetonitrile solution **(b)**: 200 μM **ANT-Fe** only (in 4:1 CH_3CN : HEPES (v/v) solution at pH = 7.0)

The effect of possible interference of all relevant cations was investigated by DPV technique, which displayed that in the presence of other cations, even with 2.5 times higher Cu^{2+} concentrations any interference was not observed (Figure 8).

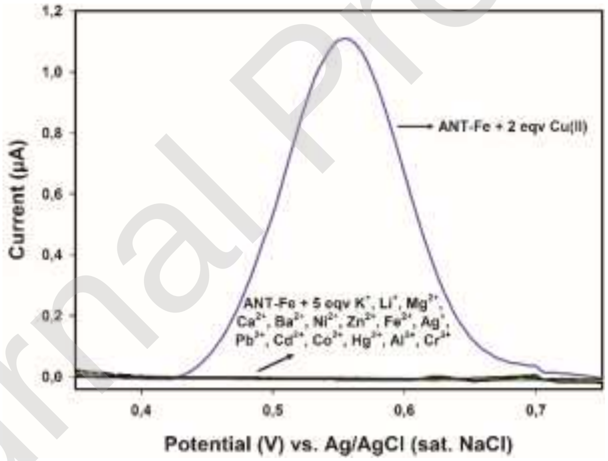


Fig. 8. DPV measurements of **ANT-Fe** and Cu^{2+} (2.0 equiv.) and other cations (2.0 equiv.) in 4:1 CH_3CN : HEPES (v/v) solution at pH = 7.0

To examine the practical applicability of **ANT-Fe**, circular test papers were prepared by immersing them into the 4:1 HEPES/CH_3CN solution at pH=7.0 containing **ANT-Fe** (10 μM), and they were dried in the air. Before the addition of any metal ions, test papers exhibited a bright green emission under UV light at 366 nm. Among all relevant metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+} (100 μM) and Cu^{2+} (50 μM), only the solution containing Cu^{2+} displayed "turn-off" response after addition onto the test papers (Figure 9b). Thus, the results exhibited that recognition of Cu^{2+} ions by **ANT-Fe** could easily be observed by the naked eye, without the need for any sophisticated instrument.

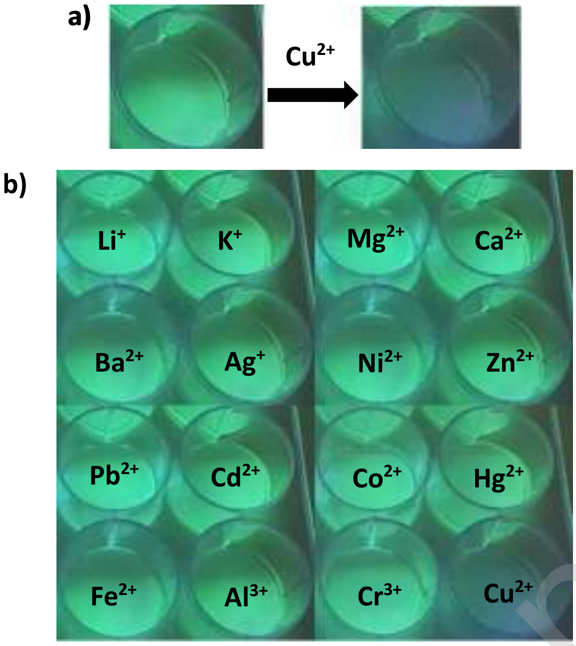


Fig. 9. (a) Fluorescence images of **ANT-Fe** adsorbed on test paper before and after addition of Cu^{2+} (50 µM) under UV light at 366 nm (b) Detection of different metal ions (100 µM) with **ANT-Fe** on TLC test paper fluorescence images under UV light at 366 nm (All images were recorded after 5 min).

4. Conclusion

In sum, we have developed a novel and easily synthesized AIE fluorescent probe (**ANT-Fe)** from commercially available two simple reagents, anthracene and ferrocenecarbaxaldehyde, where anthracene dye behaved as a fluorophore and ferrocenecarbaxaldehyde acted as a redox active unit. The probe exhibited dual sensing mode, both fluorometric “turn-off” signal mode and electrochemical signaling mode with cathodic shift, for the detection of Cu^{2+} ions in aqueous media. The sensing mechanism of **ANT-Fe** is based on the selective coordination of Cu^{2+} ions following C=N bond hydrolysis reaction. **ANT-Fe** displayed distinct features such as low detection limit (2.5 ppb), the quick response time (<30 s) as well as good selectivity toward Cu^{2+} ions over other metal ions. Also, we have successfully achieved the detection of Cu^{2+} ions with **ANT-Fe** adsorbed on the test paper system as a practical application.

CRediT authorship contribution statement

Erman Karakuş: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Simay Gunduz:** Conceptualization, Formal analysis, Investigation. **Lokman Liv:** Methodology, Formal analysis, Writing - original draft. **Turan Ozturk:** Investigation, Supervision.

Declaration of interests

Acknowledgements

The authors gratefully acknowledge TUBITAK UME for financial support and thank to Muhiddin ÇERGEL for NMR analysis, Gökhan BİLSEL for HRMS analysis and Gökhan AKTAŞ for DLS measurements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at

References

[1] D.T. Quang, J.S. Kim, Fluoro- and Chromogenic Chemodosimeters for Heavy Metal Ion Detection in Solution and Biospecimens, Chem. Rev. 110 (2010) 6280–6301.

[2] X. Chen, T. Pradhan, F. Wang, J.S. Kim, J. Yoon, Fluorescent Chemosensors Based on Spiroring-Opening of Xanthenes and Related Derivatives, Chem. Rev. 112 (2012) 1910–1956.

[3] B. Kaur, N. Kaur, S. Kumar, Colorimetric metal ion sensors – A comprehensive review of the years 2011–2016, Coord. Chem. Rev. 358 (2018) 13–69.

[4] D. Wu, A.C. Sedgwick, T. Gunnlaugsson, E.U. Akkaya, J. Yoon, T.D. James, Fluorescent chemosensors: the past, present and future, Chem. Soc. Rev. 46 (2017) 7105–7123.

[5] X. Li, X. Gao, W. Shi, H. Ma, Design Strategies for Water-Soluble Small Molecular Chromogenic and Fluorogenic Probes, Chem. Rev. 114 (2014) 590–659.

[6] R. Uauy, M. Olivares, M. Gonzalez, Essentiality of copper in humans, Am. J. Clin. Nutr. 67 (1998) 952S-959S.

[7] D.G. Barceloux, D. Barceloux, Copper, J. Toxicol. Clin. Toxicol. 37 (1999) 217–230.

[8] H. Tapiero, D.M. Townsend, K.D. Tew, Trace elements in human physiology and pathology. Copper, Biomed. Pharmacother. 57 (2003) 386–398.

[9] H. Kozlowski, A. Janicka-Klos, J. Brasun, E. Gaggelli, D. Valensin, G. Valensin, Copper, iron, and zinc ions homeostasis and their role in neurodegenerative disorders (metal uptake, transport, distribution and regulation), Coord. Chem. Rev. 253 (2009) 2665–2685.

[10] D. Plantone, G. Primiano, R. Renna, D. Restuccia, R. Iorio, K.A. Patanella, M.N. Ferilli, S. Servidei, Copper deficiency myelopathy: A report of two cases, J. Spinal Cord Med. 38 (2015) 559–562.

[11] I.A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, Synthetic models of the active site of catechol oxidase: mechanistic studies, Chem. Soc. Rev. 35 (2006) 814–840.

[12] E.L. Que, D.W. Domaille, C.J. Chang, Metals in Neurobiology: Probing Their Chemistry and Biology with Molecular Imaging, Chem. Rev. 108 (2008) 1517–1549.

[13] J. Cho, T. Pradhan, Y.M. Lee, J.S. Kim, S. Kim, A calix[2]triazole[2]arene-based fluorescent chemosensor for probing the copper trafficking pathway in Wilson's disease, Dalt. Trans. 43 (2014) 16178–16182.

[14] A.R. G. Georgopoulos M. J. Yonone-Lioy, R. E. Opiekun, P. J. Lioy, P., Environmental copper: its dynamics and human exposure issues, J. Toxicol. Environ. Heal. Part B. 4 (2001) 341–394.

[15] L.M. Gaetke, C.K. Chow, Copper toxicity, oxidative stress, and antioxidant nutrients, Toxicology. 189 (2003) 147–163.

[16] H.S. Jung, P.S. Kwon, J.W. Lee, J. Il Kim, C.S. Hong, J.W. Kim, S. Yan, J.Y. Lee, J.H. Lee, T. Joo, J.S. Kim, Coumarin-Derived Cu2+-Selective Fluorescence Sensor: Synthesis, Mechanisms, and Applications in Living Cells, J. Am. Chem. Soc. 131 (2009) 2008–2012.

[17] J. Cotruvo Joseph A., A.T. Aron, K.M. Ramos-Torres, C.J. Chang, Synthetic fluorescent probes for studying copper in biological systems, Chem. Soc. Rev. 44 (2015) 4400–4414.

[18] D. Udhayakumari, S. Naha, S. Velmathi, Colorimetric and fluorescent chemosensors for Cu2+. A comprehensive review from the years 2013–15, Anal. Methods. 9 (2017) 552–578.

[19] G. Trusso Sfrazzetto, C. Satriano, G.A. Tomaselli, E. Rizzarelli, Synthetic fluorescent probes to map

metallostasis and intracellular fate of zinc and copper, Coord. Chem. Rev. 311 (2016) 125–167.

[20] J.R. Lakowicz, Principles of fluorescence spectroscopy, Second edition. New York : Kluwer Academic/Plenum, [1999].

[21] J. Luo, Z. Xie, J.W.Y. Lam, L. Cheng, H. Chen, C. Qiu, H.S. Kwok, X. Zhan, Y. Liu, D. Zhu, B.Z. Tang, Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole, Chem. Commun. (2001) 1740–1741.

[22] M. Wang, G. Zhang, D. Zhang, D. Zhu, B.Z. Tang, Fluorescent bio/chemosensors based on silole and tetraphenylethene luminogens with aggregation-induced emission feature, J. Mater. Chem. 20 (2010) 1858–1867.

[23] J. Mei, N.L.C. Leung, R.T.K. Kwok, J.W.Y. Lam, B.Z. Tang, Aggregation-Induced Emission: Together We Shine, United We Soar!, Chem. Rev. 115 (2015) 11718–11940.

[24] S. Samanta, U. Manna, T. Ray, G. Das, An aggregation-induced emission (AIE) active probe for multiple targets: a fluorescent sensor for Zn2+ and Al3+ & a colorimetric sensor for Cu2+ and F−, Dalt. Trans. 44 (2015) 18902–18910.

[25] M. Gao, B.Z. Tang, Fluorescent Sensors Based on Aggregation-Induced Emission: Recent Advances and Perspectives, ACS Sensors. 2 (2017) 1382–1399.

[26] M. Shyamal, S. Maity, A. Maity, R. Maity, S. Roy, A. Misra, Aggregation induced emission based “turn-off” fluorescent chemosensor for selective and swift sensing of mercury (II) ions in water, Sensors Actuators B Chem. 263 (2018) 347–359.

[27] S. Mukherjee, P. Thilagar, Molecular flexibility tuned emission in “V” shaped naphthalimides: Hg(ii) detection and aggregation-induced emission enhancement (AIEE), Chem. Commun. 49 (2013) 7292–7294.

[28] E. Karakuş, An anthracene based fluorescent probe for the selective and sensitive detection of Chromium (III) ions in an aqueous medium and its practical application, Turk J Chem, (2020) DOI: 10.3906/kim-2003-41.

[29] J. Ma, C. Zhang, Y. Xiao, M. Zhang, Q. Wang, W. Zheng, S. Zhang, Preparation 2-(anthracen-9-yl)-1,3-dithiolane as a novel dual-channel AIE-active fluorescent probe for mercury (II) ion with excellent performance, J. Photochem. Photobiol. A Chem. 378 (2019) 142–146.

[30] M. Shellaiah, Y.-H. Wu, A. Singh, M. V Ramakrishnam Raju, H.-C. Lin, Novel pyrene- and anthracene-based Schiff base derivatives as Cu2+ and Fe3+ fluorescence turn-on sensors and for aggregation induced emissions, J. Mater. Chem. A. 1 (2013) 1310–1318.

[31] H. Yang, Z. Zhou, K. Huang, M. Yu, F. Li, T. Yi, C. Huang, Multisignaling Optical-Electrochemical Sensor for Hg2+ Based on a Rhodamine Derivative with a Ferrocene Unit, Org. Lett. 9 (2007) 4729–4732.

[32] Y. Fang, Y. Zhou, Q. Rui, C. Yao, Rhodamine–Ferrocene Conjugate Chemosensor for Selectively Sensing Copper(II) with Multisignals: Chromaticity, Fluorescence, and Electrochemistry and Its Application in Living Cell Imaging, Organometallics. 34 (2015) 2962–2970.

[33] V. Uahengo, B. Xiong, P. Zhao, Y. Zhang, P. Cai, K. Hu, G. Cheng, Three-channel ferrocene-based chemosensors for Cu(II) and Hg(II) in aqueous environments, Sensors Actuators B Chem. 190 (2014) 937–945.

[34] M. Li, Z. Guo, W. Zhu, F. Marken, T.D. James, A redox-activated fluorescence switch based on a ferrocene–fluorophore–boronic ester conjugate, Chem. Commun. 51 (2015) 1293–1296.

[35] J.-Z. Ge, Y. Zou, Y.-H. Yan, S. Lin, X.-F. Zhao, Q.-Y. Cao, A new ferrocene–anthracene dyad for dual-signaling sensing of Cu(II) and Hg(II), J. Photochem. Photobiol. A Chem. 315 (2016) 67–75.

[36] S.R. Bhatta, V. Bheemireddy, G. Vijaykumar, S. Debnath, A. Thakur, An Efficient Molecular Tool with Ferrocene Backbone: Discriminating Fe3+ from Fe2+ in Aqueous Media, Organometallics. 36 (2017) 2141–2152.

[37] J. Mei, Y. Hong, J.W.Y. Lam, A. Qin, Y. Tang, B.Z. Tang, Aggregation-Induced Emission: The Whole Is More Brilliant than the Parts, Adv. Mater. 26 (2014) 5429–5479.

[38] M. Shyamal, D. Das, P.K. Giri, S. Maity, A. Misra, Aggregation-induced emission–based highly selective ‘turn-off’ fluorogenic chemosensor for robust quantification of explosive picric acid in aqueous and solid states, Mater. Today Chem. 14 (2019) 100193.

[39] M. Shyamal, S. Maity, P. Mazumdar, G.P. Sahoo, R. Maity, A. Misra, Synthesis of an efficient Pyrene based AIE active functional material for selective sensing of 2,4,6-trinitrophenol, J. Photochem. Photobiol. A Chem. 342 (2017) 1–14.

[40] J. Chen, C.C.W. Law, J.W.Y. Lam, Y. Dong, S.M.F. Lo, I.D. Williams, D. Zhu, B.Z. Tang, Synthesis, Light Emission, Nanoaggregation, and Restricted Intramolecular Rotation of 1,1-Substituted 2,3,4,5-Tetraphenylsiloles, Chem. Mater. 15 (2003) 1535–1546.