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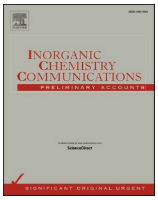

Short communication

Fluorimetric quantification of picric acid in aqueous medium via smartphone and invisible ink applications using pyrene based sensor

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ABSTRACT

A simple imidazole-pyrene based sensor **(1)** has been developed by simple one step reaction and characterized by using common spectroscopic techniques. When various nitroaromatic compounds were incorporated to CH_3CN: H_2O (1:2, v/v) solution of **1**, the fluorescent probe turned non-fluorescent in presence of picric acid, upon irradiation at 310 nm. This was accompanied by negligible changes with other molecules along with fluorescent color change from bluish-green to colorless in case of picric acid. Also, the fluorimetric sensing of picric acid was done using smartphone and invisible ink applications. The sensor has been found efficient for the recognition of picric acid in aqueous medium.

1. Introduction

Nitroaromatic compounds have been the most commonly used chemicals all around the world because of their wide applications in industries and other fields. It happens due to the unique chemistry of nitro groups, which makes the π-electrons of the ring delocalize when get attached to a benzene ring. In addition, they have deactivating nature towards the electrophilic aromatic substitution of the benzene ring due to which meta positions receive more attacks. The most exceptional application includes their use in high-energy explosives [1,2].

Because of its highly explosive nature, more toxicity than trinitrotoluene (TNT) and its extensive use during World War I, picric acid (PA) has been seen as an imminent competitor amongst diverse nitroaromatic compounds [3,4]. Additionally, it has high solubility in water, leading to the main contaminant of groundwater. It has been widely used in the dye industry, matches and leather processing, rocket fuel manufacturing, and pharmaceuticals industry [5,6]. Its exposure can result in skin and eye irritations, liver breakdown and chronic syndromes similar to anaemia, cancer and cyanosis [7–9]. As a result, responsive and careful recognition of such an explosive turns out to be an area of superlative significance in today's world. Conversely, the precise detection of PA continues to exist as a challenging and demanding job for the research fraternity owing to its electron-deficient character in contrast to the other nitroaromatic explosives.

There has been a variety of techniques for recognizing nitroaromatic explosives that involve trained canines, metal sensors, and different spectroscopic methods [10–13]. Currently, the research field of developing and creating molecules with good sensitivity and selectivity has seen a brilliant success [14,15]. Amidst them, for sensing a variety of analytes along with extensive applications in environmental chemistry, cell biology, and biochemistry, fluorescent sensors have drawn considerable attention as vibrant tools [16]. The analyses based on fluorescent sensors have different advantages such as easy sample preparation, rapid response time and highly economical [17–21]. Several fluorimetric sensors have been reported in the literature including small molecular structures, metal nanoparticles, and numerous supramolecules [22–24]. However, these mostly incorporate sensors with hydrophobic nature due to which they lack practical applications in the aqueous medium. For that reason, to recognize nitroaromatic compounds in water systems, a lot of hydrophilic sensors have been developed [25].

The recent developments in smartphone technology advanced the areas of chemical and biological sensing for a wide series of analytical species [26,27]. The technological hitches have been conquered by the means of 3D printing technology and smart software [28–30]. The primarily utilized element of a smartphone has been its camera that analyzes the color images quantitatively using colorimetry or photometry. For the spectrometers or specially framed test strip readers, colorimetric investigation has been a commonly used chemical process. Smartphone technology can assist chemists in colorimetric analysis with the captured image quantification.

Furthermore, in the present age where any information could be

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spread or leaked in many ways involving social media, the internet, and printing data [31,32], it becomes very important to follow such an approach to conceal documented data [33]. If some important information got revealed, it could pose high risks at national levels. Hence, the concept of high-security invisible ink [34,35] has been introduced these days to hide information/data and avoid significant risks to commercial and military purposes [36].

In this work, we have demonstrated the facile synthesis of fluorimetric imidazole-pyrene based sensor, **1**, which has been employed successfully for detection of picric acid (PA) in aqueous solution. In addition, the sensor has also been applied for the fluorescence color analysis of PA using smartphone based application 'Color Detector App'. Further, the concept of invisible ink has been displayed by fluorimetric changes observed upon the addition of PA in the aqueous solution of sensor, **1**.

2. Experimental

2.1. Materials and instrumentations

The detailed information about materials used for synthesis of sensor **1** and general procedure for UV–vis, fluorescence and ^{1}H NMR titration studies have been given in SI.

2.2. Synthesis of sensor (1)

The sensor **1** was developed by using the reactants, benzil and pyrene-1-carboxaldehyde, in equal ratio in glacial acetic acid (Scheme 1).

3. Results and discussion

3.1. Fluorescence spectral studies

Initially, to review the sensing competency of sensor **1**, the UV–vis spectra of the sensor **1** (20 μM) in CH_3CN:H_2O (1:2, v/v) (Fig. S5) was investigated with different nitroaromatic explosives including PA, 2-NT, 4-NT, 4-NP, NB, TNT and DNP. Keeping in mind the selectivity factor, the solvent system CH_3CN:H_2O (1:2, v/v) was employed after evaluating other solvent systems for detection of nitroaromatics. There was obtained two peaks at 270 and 359 nm in the UV spectra of the sensor **1**. Upon the incorporation of above mentioned compounds to the CH_3CN:H_2O (1:2, v/v) solution of sensor **1**, negligible changes were obtained in the absorption spectrum. Although, a new peak was observed at 359 nm, yet any definite changes observed with PA addition could not be acknowledged because of own absorbance of PA around 350 nm.

In contrast, a fluorescent behavior was exemplified by sensor **1** (λ_{ex} = 310 nm). Though, upon incorporation of various nitroaromatic compounds such as PA, 2-NT, 4-NT, 4-NP, NB, TNT and DNP, only addition of PA to the solution of **1** (2 μM; CH_3CN:H_2O (1:2, v/v)) produced remarkable quenching of fluorescence intensity (Fig. 1a). In the same environment, all other incorporated molecules demonstrated fluorescence responses of no consequence. In addition, fluorimetric color changes were detected in the presence of only PA from bluish-green to colorless, upon irradiation with light of wavelength 310 nm (Fig. 1b).

The quantitative evaluation was done for analyzing the interactions between **1** and PA using fluorescence titration experiment by the addition of PA to solution of sensor **1**. With the progressive addition of PA, the fluorescence intensity was quenched gradually with an insignificant shift in the spectra indicative of the formation of [**1**-PA] complex (Fig. 2). The quenching of fluorescence intensity might be due to π-π interactions between picric acid and pyrene moiety of sensor **1**, which disrupted the conjugated system. It was also scrutinized that PA itself demonstrated a weak emission peak at around 372 nm in the fluorescence spectra and this peak did not interfere in the given spectral changes. Hence, the responses observed are caused due to complex formation of [**1**-PA] after their interactions in excited state.

The job's plot revealed the 1:1 binding stoichiometric ratio of sensor **1** with PA (Fig. S6) with association coefficient of 2.13 × 10^4 M^{-1} computed on the basis of fluorescence titrations by use of the Benesi-Hildebrand equation given below [37];

$$1/F - F_o = 1/F_{max} - F_o + 1/[F_{max} - F_o]K[C]$$

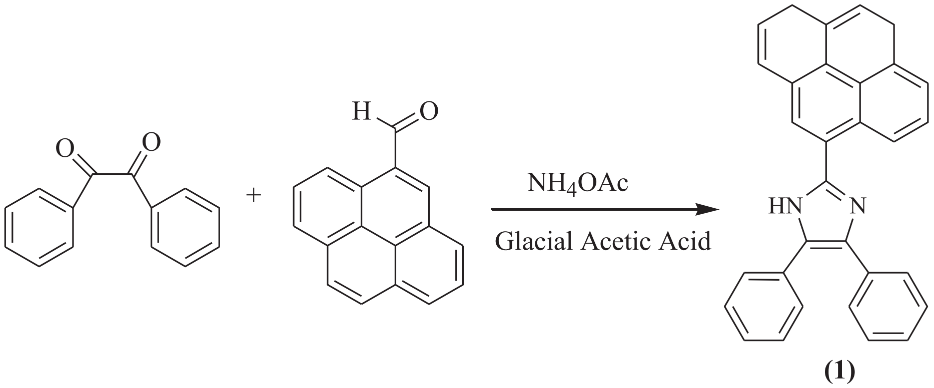
here, F_o = fluorescence of free sensor **1**, F = fluorescence measured with PA and F_{max} = emission intensity value estimated with an excess amount of PA at 470 nm; K = association coefficient and [C] = PA concentration added.

Assessment of the limit of detection (LOD) was done by employing the equation: LOD = 3σ/s [38] and it was estimated as 8.14 × 10^{-7} M.

There has been an implication of the selective detection of PA amongst other said nitroaromatic compounds by using sensor **1** on the basis of above results.

3.2. ^{1}H NMR titration experiment

For assessing the optical responses and type of interactions upon the addition of PA in sensor **1**, ^{1}H NMR titration experimentation was implemented (Fig. S7). When 0.5 equiv. of PA was added, the signal of aromatic protons in the free sensor **1** from δ 8.5–7.5 ppm was shifted slightly upfield and there was appearance of a new peak respective of picric acid (PA) at around δ 8.65 ppm after the incorporation of 1.0 equiv. of PA. These outcomes unveiled the interactions of PA with the pyrene aromatic protons and hence, the NMR peaks were moved to the shielded area attributable to disturbance in the conjugation of the pyrene ring.



(1)

Scheme 1. Synthesis of the target sensor **1**.

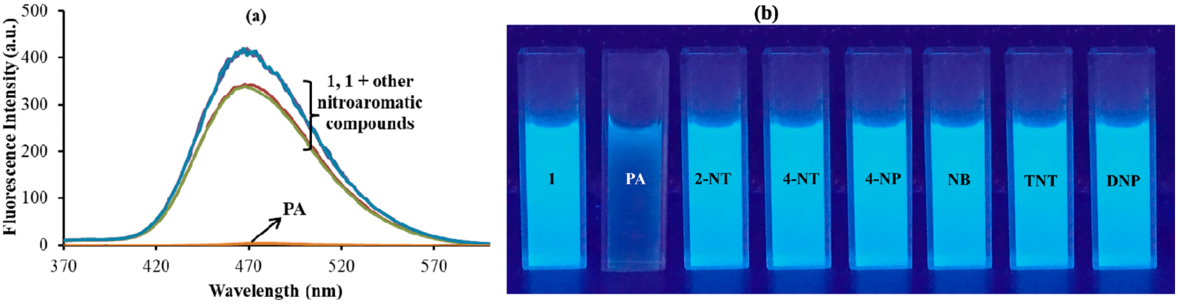


Fig. 1. (a) Fluorescence response of **1** in CH_3CN:H_2O (1:2, v/v) upon addition of 100 equiv. of different nitroaromatic compounds; (b) Fluorescent colorimetric responses of **1** in CH_3CN:H_2O (1:2, v/v) in the presence of 100 equiv. of above said nitroaromatics.

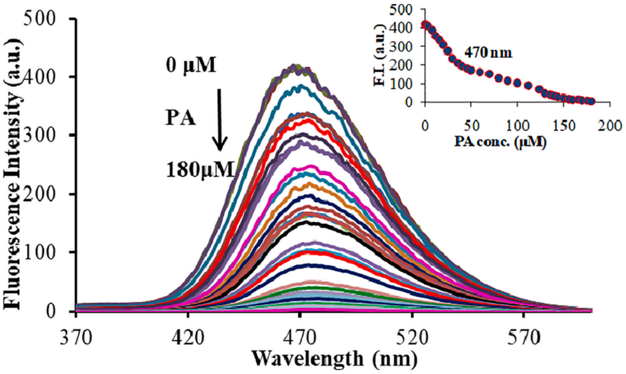


Fig. 2. Fluorescence titration spectra of **1** (2 μM) in CH_3CN:H_2O (1:2, v/v) by incorporating different concentrations of PA (λ_{ex} = 310 nm). Inset: Emission intensity curve at 470 nm versus the concentration of added PA.

3.3. DFT calculations

The theoretical studies were carried out for the estimation of the structural and binding characteristics of sensor **1** with PA. The optimization of the structures of sensor **1** and **1**-PA complex (1:1) were performed by Density Functional Theory method (DFT). These calculations were executed using the Gaussian 03 package using the exchange correlation function B3LYP and the basis set 6–31G (d, p) for C, H, N, and O atoms. Figure S8 displayed the optimized structures of **1** and the **1**-PA complex along with the energy consideration diagram which presented that on complex formation of **1** with PA molecule, the energy gap of HOMO and LUMO decreased with respect to free sensor pointing towards the formation of a stable conjugate. Also, it has been observed that the bond distance between the pyrene group and the –OH of PA was decreased from 3.26 Å (in input file) to 2.98 Å (in output file) in the 1-PA complex and there was witnessed a small decrease in the distance amid the pyrene moiety and -NO_2 (of PA) from 3.04 Å (in input file) to 2.8 Å (in output file) (Fig. S9). These observations evidently advocated the interactions between the PA molecule and pyrene group of sensor **1** and corroborated with absorption and fluorescence changes.

Additionally, the electron density of the HOMO of **1** was situated on the electron withdrawing as well as electron donating part and for the LUMO, the electron density lied on the electron donating portion. The DFT plots of the HOMO, and LUMO after the addition of PA presented that the electron density was located on the electron-withdrawing area of sensor **1**, and on the PA fragment, respectively (Fig. S8).

3.4. Interference studies

For establishing a sensor’s performance, its highly selective nature for the target species amongst other interfering species has been a significant aspect. Consequently, in the presence of 50 equiv. of PA assorted with 100 equiv. of various competing nitroaromatic compounds (2-NT, 4-NT, 4-NP, NB, TNT and DNP), interference studies were conducted by means of fluorescence spectroscopy. Also, the competitive studies were carried out with 100 equiv. of common anions and metal ions mentioned above. Figure S10a-S10b clearly demonstrated that the fluorescence responses were not influenced by the incorporation of an excess of other interfering molecules or ions. Consequently, it was suggested that sensor **1** was capable of sensing PA with great selectivity and sensitivity.

3.5. Probable recognition mechanism

The proposed sensing mechanism for detection of PA using sensor **1** has been displayed in Scheme 2, which comes into picture on the basis of optical (absorption and fluorescence studies), job’s plot titrations, computational assessments and ^{1}H NMR titration experiments. The sensor **1** comprised of a large delocalized π-system due to the presence of the conjugated planar structure of pyrene that promoted the PA molecule for interacting and binding with the pyrene group via π−π interactions and hence interfering in the conjugated arrangement, which consecutively quenched the fluorescence of sensor **1**. Here, the pyrene group took part in π−π interaction and contributed to binding of PA with 1:1 stoichiometric ratio (Scheme 2). The mechanism has been predicted to be dynamic as the formation of complex [**1**-PA] occurred in excited state only (as seen from fluorescence spectra) and also, quenching efficiency increased with rise in temperature (Fig. S11) [39]. These outcomes clearly pointed towards the probability of dynamic quenching mechanism.

3.6. Practical applications

3.6.1. Smartphone-assisted quantification of picric acid

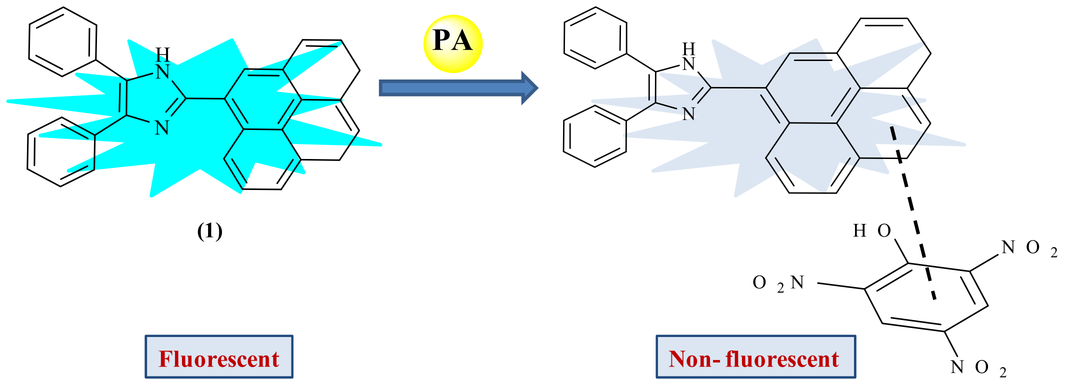
Upon the addition of picric acid (PA), the aberration in the RGB color strength of sensor **1** was determined by smartphone (Model: Redmi Y2) using ‘Color Detector App’. Sensor **1** displayed an evident fluorescent color response with PA. The RGB color values acquired from the interactions of sensor **1** with the known concentration of PA (0 to 10 μM) were recorded by the smartphone camera under UV lamp (Fig. S12a). The standard curve showing R/G ratio versus different concentrations of PA has been validated in figure S12b.

3.6.2. Practical utility-Invisible ink

The sensor **(1)** solution could be used as invisible security ink due to observable and significant fluorimetric responses in the presence of PA. It could be seen from the figure S13 that the bluish-green fluorescent color of ‘Picric Acid’ written by sensor **(1)** solution noticed under UV lamp turned non-fluorescent (colorless) with the addition of PA solution.

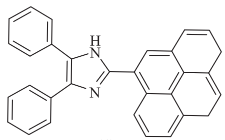
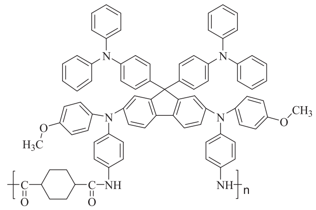
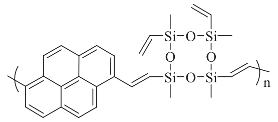
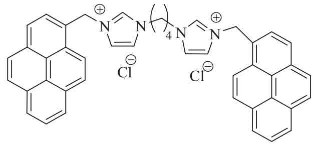
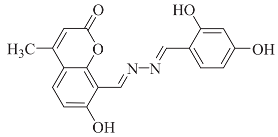
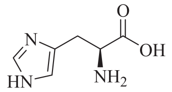
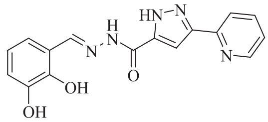
3.7. Comparison of present work with literature sensors for picric acid (PA)

The Table 1 has been formulated to compare the present work with



Scheme 2. Anticipated recognition mechanism for sensor **1** with PA.

Table 1
Comparison with the earlier reported sensors.

S.No.	Sensor	Analytes	Method for detection of Picric acid (PA)	LOD_{PA} (M)	Reference
1.	 (1)	Picric Acid	Fluorescence	8.14×10^{-7}	[Present work]
2.		Picric Acid	Absorption, Fluorescence and Electrochemical	3.2×10^{-6}	[11]
3.		Picric Acid and Trinitrotoluene	Fluorescence	–	[12]
4.		Picric Acid and PYX Explosives	Absorption and Fluorescence	1.0×10^{-6}	[40]
5.		Cu^{2+} and Picric Acid	Fluorescence	9.5×10^{-6}	[41]
6.		Picric Acid and p-Nitrophenol	Fluorescence	2.71×10^{-6}	[42]
7.		Al^{3+} and Picric Acid	Fluorescence	1.225×10^{-4}	[43]

the previously developed sensors for picric acid (PA) in literature. This has been realized that sensor **(1)** has high sensitivity and selectivity for PA recognition in contrast to the other systems. The LOD value for PA has been detected as the lowest from the analogous sensors in the literature. It has been noticed that in most of the systems (Table 1), PA interacted with sensor moieties via some functional groups present in their respective structures. While, in sensor **1**, PA molecule disturbed the conjugation of pyrene through π−π interactions, hence, quenched its fluorescence intensity. Moreover, sensor **1** has been utilized as real-time fluorimetric system for the sensing of PA using smartphone and invisible ink applications. Consequently, sensor **1** turned out to be better than the other systems owing to its simple one-pot synthetic procedure, lower detection limit and practical utilizations.

4. Conclusions

For the selective sensing of picric acid (PA) in water system, a pyrene-based fluorescent sensor **(1)** has been developed. The PA when added to the solution of sensor **1**, made it non-fluorescent by quenching the fluorescence intensity along with the fluorescent color from bluish-green to colorless. The computational calculations and job's plot titrations confirmed the recognition mechanism and the stoichiometric ratio between the sensor and the analyte. The sensor has been employed for fluorimetric color detection of PA by means of smartphone application 'Color detector App'. Moreover, the sensor could be applied in daily-life for the detection of PA by the means of invisible ink applications.

CRediT authorship contribution statement

Gitanjali Jindal: Conceptualization, Data curation, Formal analysis, Visualization, Writing – original draft. **Navneet Kaur:** Methodology, Writing – review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2022.109481.

References

[1] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental organic chemistry, second ed., Wiley-Interscience New York, NY, 2002.

[2] K.-S. Ju, R.E. Parales, Nitroaromatic Compounds, from Synthesis to Biodegradation, Microbiol. Mol. Biol. Rev. 74 (2010) 250–272.

[3] G.V. Perez, A.L. Perez, Organic Acids without a Carboxylic Acid Functional Group, J. Chem. Educ. 77 (2000) 910–915.

[4] J. Akhavan, The Chemistry of Explosives, third ed., RSC (2011).

[5] C. Beyer, U. Böhme, C. Pietzsch, G. Roewer, Preparation, characterization and properties of dipolar 1,2-N, N-dimethylaminomethylferrocenylsilanes, J. Organomet. Chem. 654 (2002) 187–201.

[6] E. Bingham, B. Cohrssen, C.H. Powell, Patty's Toxicology, John Wiley & Sons, New York, 2000, p. IIB 980..

[7] Safety data sheet for Picric Acid, Resource of National Institute of Health.

[8] P.C. Ashbrook, T.A. Houts, ACS. Div. Chem. Health Safety 10 (2003) 27–125.

[9] M. Cameron, Picric Acid Hazards, American Industrial Hygiene Association, Fairfax, VA, 1995.

[10] G. Sathiyan, B. Balasubramaniam, S. Ranjan, S. Chatterjee, P. Sen, A. Garg, R. K. Gupta, A. Singh, A novel star-shaped triazine-triphenylamine-based fluorescent chemosensor for the selective detection of picric acid, Mater. Today Chem. 12 (2019) 178–186.

[11] S. Xia, Y. Gao, P. Wang, Y. Ma, D. Zhu, H. Niu, T. Zhou, W. Wang, X. Zhao, Three dimensional fluorene-based polyamides facile to transfer ion designed for near-infrared electrochromic application and detection for explosive, Chem. Eng. J. 437 (2022) 135108.

[12] Z. Gou, A. Wang, M. Tian, Y. Zuo, Pyrene-based monomer-excimer dual response organosilicon polymer for selective detection of 2,4,6-trinitrotoluene (TNT) and 2,4,6- trinitrophenol (TNP), Mater. Chem. Front. 6 (2022) 607–612.

[13] K. Yang, Z.X. Chen, Y.J. Zhou, Q. Chen, S.W. Yu, S.H. Luo, Z.Y. Wang, Simple inorganic base promoted polycyclic construction using mucohalic acid as C_3 synthon: Synthesis and AIE probe application of benzo[4,5]imidazo[1,2-a] pyridines, Org. Chem. Front. 9 (2022) 1127–1136.

[14] K. Velmurugan, S. Mathankumar, S. Santoshkumar, S. Amudha, R. Nandhakumar, Specific fluorescent sensing of aluminium using naphthalene benzimidazole derivative in aqueous media, Spectrochim. Acta A 139 (2015) 119–123.

[15] W. Cao, X.J. Zheng, D.C. Fang, L.P. Jin, Metal ion-assisted ring-opening of a quinazoline-based chemosensor: detection of copper(II) in aqueous media, Dalton Trans. 44 (2015) 5191–5196.

[16] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J. T. Rademacher, T.E. Rice, Signaling Recognition Events with Fluorescent Sensors and Switches, Chem. Rev. 97 (1997) 1515–1566.

[17] J.S. Kim, D.T. Quang, Calixarene-Derived Fluorescent Probes, Chem. Rev. 107 (2007) 3780–3799.

[18] S.E. Angell, C.W. Rogers, Y. Zhang, M.O. Wolf, W.E. Jones, Hemilabile coordination complexes for sensing applications, Coord. Chem. Rev. 250 (2006) 1829–1841.

[19] C.W. Rogers, M.O. Wolf, Luminescent molecular sensors based on analyte coordination to transition-metal complexes, Coord. Chem. Rev. 233–234 (2002) 341–350.

[20] 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.

[21] B. Gogoi, N. Sen Sarma, Curcumin-cysteine and curcumin-tryptophan conjugate as fluorescence turn on sensors for picric acid in aqueous media, ACS Appl. Mater. Interfaces 7 (2015) 11195–11202.

[22] P. Wu, X.P. Yan, Doped quantum dots for chemo/biosensing and bioimaging, Chem. Soc. Rev. 42 (2013) 5489–5521.

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

[24] V. Bhalla, A. Gupta, M. Kumar, D.S. Rao, S.K. Prasad, Self-Assembled Pentacenequinone Derivative for Trace Detection of Picric Acid, ACS Appl. Mater. Interfaces 5 (2013) 672–679.

[25] S.C. Deshmukh, S. Rana, S.V. Shinde, B. Dhara, N. Ballav, P. Talukdar, Selective Sensing of Metal Ions and Nitro Explosives by Efficient Switching of Excimer-to-Monomer Emission of an Amphiphilic Pyrene Derivative, ACS Omega 1 (2016) 371–377.

[26] (a) D.C. Christodouleas, A. Nemiroski, A.A. Kumar, G.M. Whitesides, Broadly available imaging devices enable high-quality low-cost photometry, Anal. Chem. 87 (2015) 9170–9178;
(b) H. Rao, W. Liu, K. He, S. Zhao, Z. Lu, S. Zhang, M. Sun, P. Zou, X. Wang, Q. Zhao, Y. Wang, T. Liu, Smartphone-based fluorescence detection of Al3+ and H2O based on the use of dual-emission biomass carbon dots, ACS Sustainable Chem. Eng. 8 (2020) 8857–8867.

[27] A. Roda, E. Michelini, L. Cevenini, D. Calabria, M.M. Calabretta, P. Simoni, Integrating biochemiluminescence detection on smartphones: mobile chemistry platform for point-of-need analysis, Anal. Chem. 86 (2014) 7299–7304.

[28] J.C. Contreras-Naranjo, Q. Wei, A. Ozcan, Mobile phone-based microscopy, sensing, and diagnostics, IEEE J. Sel. Top. Quantum Electron. 22 (2016) 1–14.

[29] (a) K.E. McCracken, J.Y. Yoon, Recent approaches for optical smartphone sensing in resource-limited settings: a brief review, Anal. Methods 8 (2016) 6591–6601;
(b) S. Banik, S.K. Melanthota, J.M. Arbaaz, V.M. Vaz, I. Kadambalithaya, S. Hussain, N.M. Dutta, Recent trends in smartphone-based detection for biomedical applications: a review, Anal. Bioanal. Chem. 413 (2021) 2389–2406.

[30] M. Zangheri, L. Cevenini, L. Anfossi, C. Baggiani, P. Simoni, F.D. Nardo, A. Roda, A simple and compact smartphone accessory for quantitative chemiluminescence-based lateral ow immunoassay for salivary cortisol detection, Biosens. Bioelectron. 64 (2015) 63–68.

[31] K. Marshall, C.S. Jacobsen, C. Schäfermeier, T. Gehring, C. Weedbrook, U. L. Andersen, Continuous-Variable Quantum Computing on Encrypted Data, Nat. Commun. 7 (2016) 13795–13801.

[32] M. Dijkstra, H.E.J.J.M. Buijtels, W.F. van Raaij, Separate and Joint Effects of Medium Type on Consumer Responses: A Comparison of Television, Print, and the Internet, J. Bus. Res. 58 (2005) 377–386.

[33] P. She, Y. Ma, Y. Qin, M. Xie, F. Li, S. Liu, W. Huang, Q. Zhao, Dynamic Luminescence Manipulation for Rewritable and Multi-Level Security Printing, Matter 1 (2019) 1644–1655.

[34] Z. Song, T. Lin, L. Lin, S. Lin, F. Fu, X. Wang, L. Guo, Invisible Security Ink Based on Water-Soluble Graphitic Carbon Nitride Quantum Dots, Angew. Chem. Int. Ed. 55 (2016) 2773–2777.

[35] Y. Liu, L. Zhou, Y. Li, R. Deng, H. Zhang, Highly fluorescent nitrogen-doped carbon dots with excellent thermal and photo stability applied as invisible ink for loading important information and anticounterfeiting, Nanoscale 9 (2017) 491–496.

[36] C. Zhang, B. Wang, W. Li, S. Huang, L. Kong, Z. Li, L. Li, Conversion of Invisible Metal-Organic Frameworks to Luminescent Perovskite Nanocrystals for Confidential Information Encryption and Decryption, Nat. Commun. 8 (2017) 1138–1146.

[37] H.A. Benesi, J.H. Hildebrand, A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, J. Am. Chem. Soc. 71 (1949) 2703–2707.

[38] G.L. Long, Limit of detection. A closer look at the IUPAC definition, Anal. Chem. 55 (1983) 712A–724A.

[39] (a) J. Wang, D. Wang, D. Moses, A.J. Heeger, Dynamic Quenching of 5-(2*-Ethyl-hexyloxy)-p-Phenylene Vinylene (MEH-PPV) by Charge Transfer to a C60 Derivative in Solution, J. Appl. Polymer Sci. 82 (2001) 2553–2557;
(b) B. Pan, Y. Liu, D. Xiao, F. Wu, M. Wu, D. Zhang, B. Xing, Quantitative identification of dynamic and static quenching of ofloxacin by dissolved organic matter using temperature-dependent kinetic approach, Environ. Pollut. 161 (2012) 192–198.

[40] L. Ding, Y. Bai, Y. Cao, G. Ren, G.J. Blanchard, Y. Fang, Micelle-Induced Versatile Sensing Behavior of Bispyrene-Based Fluorescent Molecular Sensor for Picric Acid and PYX Explosives, Langmuir 30 (2014) 7645–7653.

[41] P.P. Soufeena, T.A. Nibila, K.K. Aravindakshan, Coumarin based yellow emissive AIEE active probe: A colorimetric sensor for Cu^{2+} and fluorescent sensor for picric acid, Spectrochim. Acta A Mol. Biomol. Spectrosc. 223 (2019) 117201.

[42] R. Patel, S. Bothra, R. Kumar, S.K. Sahoo, Selective turn-off sensing of picric acid and *p*-nitrophenol using fluorescent histidine, Nano-Struct. Nano-Objects 19 (2019) 100345.

[43] S. Saha, A. De, A. Ghosh, A. Ghosh, K. Bera, K.S. Das, S. Akhtar, N.C. Maiti, A. K. Das, B.B. Das, R. Mondal, Pyridine-pyrazole based Al(III) ‘turn on’ sensor for MCF7 cancer cell imaging and detection of picric acid, RSC Adv. 11 (2021) 10094–10109.