

1, 3, 6, 8-pyrene sulfonic acid tetrasodium fluorescent pigment synthesis and security ink production

ABSTRACT

Colorants used in security inks are special pigments that radiate in the UV region or IR region. Obtained pigments can be from valuable rare earth elements or they can be organic based. Organic-based pigments are generally insoluble in water, which limits their use. For this purpose, an organic-based UV-radiating pigment was synthesized and made water-soluble by forming its salt. With the obtained salt-formed pigment, inkjet ink that can be used in counterfeiting was applied and its printability and resistance properties were determined. In this study, 1, 3, 6, 8-pyrene sulfonic acid tetrasodium salt was synthesized and water-based inkjet inks with hydroxy ethyl cellulose binder were produced. The prepared inks were printed on the paper surface. The color and gloss of the prints obtained were measured both in the visible region and in the UV region. Its optical properties were detected by UV spectroscopy. Strength properties such as light fastness, nitro resistance, alkali resistance, acid resistance, rub resistance, drying time, adhesion and dry film weight of the prints were determined. As a result; Inkjet ink with 1, 3, 6, 8-pyrene sulfonic acid tetrasodium salt was produced and it was concluded that it has good resistance properties.

KEY WORDS

Anti-counterfeiting, security ink, resistance, printability, water soluble ink

Emine Arman Kandirmaz 
Arif Ozcan 

Marmara University, Faculty of Applied Sciences, Department of Printing Technologies, Istanbul, Turkey

Corresponding author:
Emine Arman Kandirmaz
e-mail: earman@marmara.edu.tr

First received: 16.6.2023.

Revised: 22.9.2023.

Accepted: 3.10.2023.

Introduction

Security inks are used on important documents, labels and cards. security inks can be printed as a top varnish or added to the lamination to protect them from counterfeiting. these inks absorb light in one area and emit it in another, but for such inks to work properly, there must be no UV brightener in the substrate. Although anti-counterfeiting is mostly seen in money and passports in daily life, it is actually used in many fields from military to pharmacy. The use of secure information transfer is one of the techniques that reduces counterfeiting. Among the stimulus-sensing materials, there are photoluminescent materials. While these materials are not visible in visible light, their optical outputs can change under a different stimulus light. Thus, the image appears only under the desired light, which enables the product to be read only by those who will access the data. Security inks are frequently used for these applications (Song et al., 2016).

Organic fluorescent dyes are the most commonly used types in security inks as photoluminescent material. however, such colorants have low photostability (Pham et al., 2004). Apart from these, Conjugated polymers dots (Chang et al., 2014) and inorganic quantum dots are used with narrow and adjustable working bandwidths. Recently, photoluminescent materials radiating in the near infrared region have been used in areas where high security requirements are required (Sun et al., 2012).

Although organic fluorescent safety pigments are frequently encountered, one of the problems in use is that they do not dissolve in water and choose solvents. The use of colorant in ready-made ink varnish in ink production both facilitates production and reduces investment costs. For this reason, it is desired that the safety pigment produced is compatible with the ready-made varnish used in production. Organic fluorescent materials that have dissolution and dispersion problems are being improved in this regard.

Thanks to pyrene π -bonds, it has a rigid structure with good fluorescence properties and fast response stability better than some other organic fluorescent materials (Sonar et al., 2010). It attracts attention with these features (Chakraborty, Chakraborty & Das, 2018). There are studies in the literature to increase the water solubility of pyrene (Miskolczy et al., 2018; Khan, Ramu & Pitchumani, 2018).

As in printing with conventional inks, security inks are required to be compatible with the substrate, to have maximum resolution, to remain on the substrate for a long time without any problems, to be unaffected by sunlight and environmental conditions, or to have minimum color and effect changes. These printability properties can be listed as light fastness, nitro resistance, alkali resistance, acid resistance, rub resistance, drying time, adhesion and dry film weight of the prints etc (Leelajariyakul, Noguchi & Kiatkamjornwong, 2008). These features determine both the printing technique of the ink, the place of use and the life of the printed product, and also affect the cost.

In this study, 1, 3, 6, 8-pyrene sulfonic acid tetrasodium fluorescent safety pigment was synthesized and structurally and optically illuminated. Inkjet ink was produced using hydroxy ethyl cellulose with the obtained pigment and printed with a thermal inkjet printing machine. The printability properties of the produced prints were investigated. As a result, it has been determined that the fluorescent ink is invisible in daylight, but appears blue under UV light, has good printability properties and can be used in security inks.

Experimental

Materials

Pyrene, fumed sulphuric acid, nitrobenzene, calcium hydroxide, sodium carbonate, n-butanol and hydroxy ethyl cellulose were purchased from Sigma-Aldrich (Taufkirchen, Germany). Printed paper was purchased from UPM-Kymmene Corporation (Helsinki, Finland). The properties of the paper used are added to Table 1.

Methods

1,3, 6, 8-pyrene sulfonic acid tetrasodium salt has been synthesized to be used in ink. First of all, 8 mmol of pyrene and 30 mL of nitrobenzene were loaded into a single-necked reaction flask, and homogeneous distribution was achieved by mixing. Then, 5 mL of fumed sulphuric acid was added dropwise to the reaction flask. The mixture was stirred overnight keeping the temperature constant at 30 °C. then the temperature was raised to 60 °C. The mixture, which was stirred rapidly at 1000 rpm for one day at this temperature, was poured into ice-wa-

Table 1

Properties of the paper used in the printing

Features	Standard	Uncoated Paper
Grammage (g/m ²)	ISO 536	120.0
Thickness (μm)	TAPPI T 411	107
Bulk (cm ³ /g)	ISO 534:1995	1.25
Whiteness (CIE D65/10) (%)	ISO 11475	146
Brightness (D65/10) (%)	ISO 2470-2	82.3
Opacity (D65/10) (%)	ISO 2471	96.5
Gloss (TAPPI 75) (%)	T480 om-92	6
Air permanence (Bendtsen) (μm/Pa-s)	ISO 5636/3	5.610

ter and calcium hydroxide was added to the medium as a neutralizing agent. The obtained product was filtered and sodium carbonate was added at an equivalent rate to sulfuric acid. The product, washed with n-butanol to remove unreacted nitro benzene, was evaporated at 75 °C and dried in a vacuum oven at room temperature for 24 hours. The chemical structure of the synthesized substance was elucidated by ¹H-NMR (Chen et al., 2019).

Inkjet ink was produced using the produced fluorescent pigment. For this, 0.5% (w/v) hydroxy ethyl cellulose water mixture was prepared and stirred at 250 rpm for 15 minutes at 90 °C until it became clear. The resulting mixture was cooled to 45 °C. 0.5 mg/ml of 1, 3, 6, 8-pyrene sulfonic acid tetrasodium salt was added to the mixture produced into the cooled mixture and stirred at room temperature for half an hour to obtain a homogeneous mixture. The viscosity of the ink is 4 mPa s. adjusted with water. The obtained ink was printed on the uncoated paper surface with the BENTSAI BTHH 6105 handheld thermal inkjet printing machine. Refillable cartridge with 42 mL ink capacity, 300 DPI printing resolution, printing speed 250 mm/s, printing delay 10 mm, cartridge voltage 10-12 V and the total nozzle number 54 are the parameters of thermal inkjet printing machine.

Characterization

¹H-NMR spectra were performed with using a Varian Unity Inova Spectrometer (CAL USA) operated at 400 MHz frequency. The color measurements of prints were made by CIE L*, a*, b* method using X-Rite eXact spectrophotometer according to ISO 12647-2: 2013 standard. The measurement conditions of the spectrophotometer are determined as polarization filter with 0° / 45° geometry with 2° observer angle with D50 light source in the range of 400-700 nm.

The difference between the colors of the different prints were calculated according to the CIE ΔE 2000 color-difference formula (1) ISO 11664-6:2014. Calculations were made by taking the average of five measurements. ΔL*, Δa*, Δb*: Difference in L*, a*, and b* values between specimen color and target color. Lightness is

represented by the L* axis which ranges from white to black. The red area is connected to the green by the a* axis, while the b* axis runs from yellow to blue.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2} + R_T \frac{\Delta C'}{k_C S_C} \frac{\Delta H'}{k_H S_H} \quad (1)$$

where ΔL^* , ΔC^* , and ΔH^* are the CIEL*a*b* metric lightness, chroma, and hue differences, respectively, calculated between the standard and sample in a pair, ΔR is an interactive term between chroma and hue differences. The S_L , S_C , and S_H are the weighting functions for the lightness, chroma, and hue components, respectively. The values calculated for these functions vary according to the positions of the sample pair being considered in CIEL*a*b* color space. The k_L , k_C , and k_H values are the parametric factors to be adjusted according to different viewing parameters such as textures, backgrounds, separations, etc., for the lightness, chroma, and hue components, respectively (Bates, Džimbeg-Malčić & Itrić, 2012).

The gloss was measured with BYK Gardner GmbH BYK Gardner GmbH micro Tri-gloss 60° geometry in accordance with ISO 2813:2014. The print was subjected to the light fastness test to determine how the color would change over time in the ground prints. In the light fastness test, all prints made with a blue wool scale were kept in a UV light cabinet for 192 hours, the initial and final CIEL*a*b* values were measured and how much the color changed according to BS4321 standard. Photographs of the printed products were taken with the Nikon D5300 camera using the UV-IR-cut filter.

Tesa-tape was used in the adhesion test, which is used to determine the interaction between the ink and the surface. In this method, the tape cut in a certain size is adhered to the printed surface and pulled quickly at an angle of 90°. After the tape separated from the surface was adhered to a white paper, visual examination was made under visible and UV light. The test was repeated 3 times. The rub resistance of the printed paper is made according to the ASTM D 5264 standard. After waiting for 2 days for the printed paper to dry completely, the test was carried out with a Sutherland Ink Rub Tester (San Antonio, Texas) at 920 g load, 30 oscillations measurement conditions. Rub resistance-treated specimens were visually inspected under UV and visible light.

The method in the literature was used to measure the drying time (Carreira, Agbezuge & Gooray, 1995). After Solid tone printing is made with the produced ink, clean paper is covered and stretched between two cylinders with 350 N pressure. Ink on clean paper shows the remaining ink before it dries. Clean paper is visually inspected under both daylight and UV light. It is selected when there is no ink transfer to the clean paper during the full drying period. While determining the dry film weight of the printed ink, uncoated paper was first weighed (T1). 100 cm (A) solid tone was

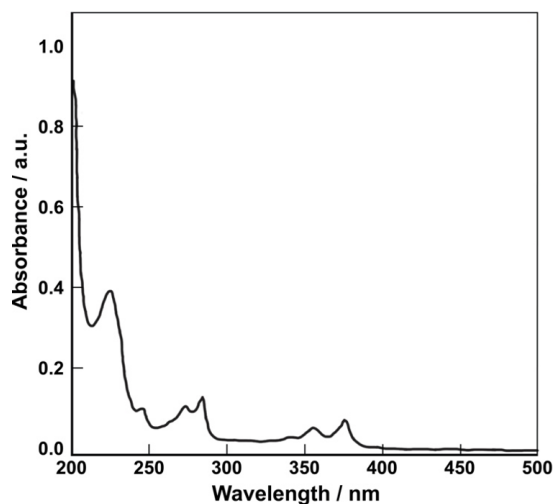
printed on this paper and weighed (T2). The dry ink weight was calculated with the following formula.

$$\text{Dry Ink Film Weight} = \frac{(T_2 - T_1)10000}{A} \quad (2)$$

The nitro, acid and alkali resistance of produced ink was performed as in the literature according to QB 568–1983 standard (Chen, Li & Chen, 2021).

Results and Discussion

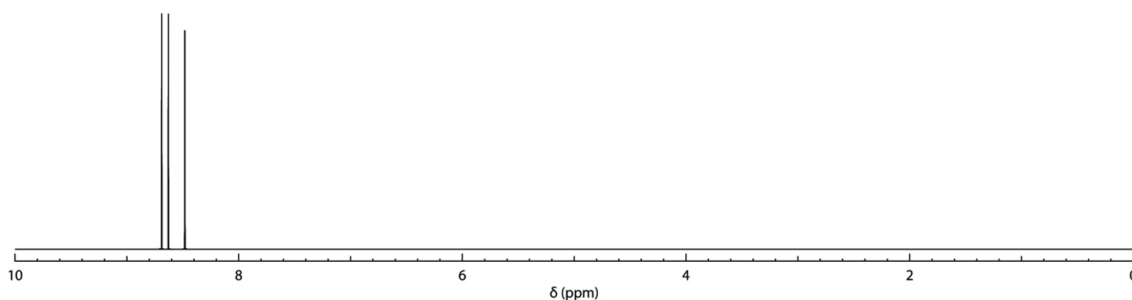
1, 3, 6, 8-pyrene sulfonic acid tetra sodium salt was examined by UV-vis spectroscopy of and is given in Figure 1. When Figure 1 is examined, two main absorption bands belonging to the p-p transition in pyrene are seen, as it is said in the literature (Costa et al., 2015). The first of these is the exciting state at 285 nm, and the other is the emission state at 400 nm.



» **Figure 1:** UV-Vis spectrum of 1, 3, 6, 8-pyrene sulfonic acid tetra sodium in water.

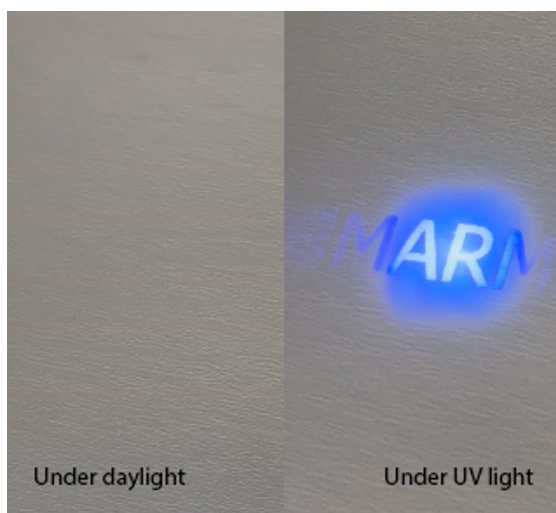
The chemical structure of the obtained 1, 3, 6, 8-pyrene sulfonic acid tetra sodium molecule was elucidated by ¹H NMR and given in Figure 2. When Figure 2 is examined, peaks belonging to two hydrogens are seen at 8.48 ppm and peaks belonging to 4 hydrogens at 8.66 ppm. This indicates that the molecule has been successfully synthesized. In addition, the results are in line with the literature (Rodenburg et al., 1988).

It has been determined that 1, 3, 6, 8-pyrene sulfonic acid tetrasodium can be easily dispersed both in water and in hydroxyethyl cellulose, and the resulting mixtures are transparent-white. The prepared inks were kept for sixty days and at the end it was determined that 1, 3, 6, 8-pyrene sulfonic acid tetrasodium was still homogeneously dispersed. The prepared ink has a homogeneous structure, and there is no settling problem up to a resolution of 1 mg/ml. No precipitation was observed depending on the temperature change in the



» **Figure 2:** ^1H NMR spectrum of 1, 3, 6, 8-pyrene sulfonic acid tetra sodium in water

environment. The resulting inks were printed on a UV blocker-free paper surface and their images were examined in both visible and UV light. The results are given in Figure 3. When Figure 3 was examined, it was determined that there was no image on the printed paper in daylight, only the blue bright image was easily visible at 365 nm under UV light. This shows that the printed image keeps the information in daylight and makes it visible under a special light source, that is, the ink produced can be used in security prints. The results are in line with the literature (Yao et al., 2017; You et al., 2015).



» **Figure 3:** Fluorescent ink printed surfaces photographs at under daylight and UV light

Printability tests such as color, gloss, light fastness, adhesion, rub resistance, drying time, dry ink film weight, alkali, acid and nitro resistance were applied to the obtained security ink printed samples and the results are given in Table 2.

When Table 2 is examined; While printing under daylight shows that there is a white image in L^* , a^* , and b^* values, there is no image, while the change in b^* and a^* values under UV light shows blue color. When examined in terms of gloss, a very glossy surface was obtained compared to the base paper. Because the spaces between the cellulose fibers are filled and a more gloss surface is obtained with less light scattering (Arman Kandirmaz et

al., 2020). It has been concluded that the security ink, which has a light fastness of 7, can be used for two years without any problem on the exterior, where it is highly resistant to light.

Table 2

Printability test of security ink

Printability tests	Results			
	L^* : 100	a^* : 0	b^* : 1	
Color (Daylight)	L^* : 91	a^* :-13	b^* :-11	ΔE_{00} :16.37
Gloss	11.2			
Light fastness	7			
Adhesion	5 (excellent)			
Rub resistance	1 (excellent)			
Drying time	4 sec			
Dry ink film weight	2.5 g/m ²			
Alkali resistance	✓			
Acid resistance	✓			
Nitro resistance	✓			

When the adhesion of the prints made with this ink is examined, it has been observed that no ink residues have passed onto the tape in all printed samples from 4 seconds after printing, both in visible light and UV light. In other words, it was determined that it had high adhesion. When examined in terms of rub resistance, it was determined that there was no scratch on the surface at the end of 30 oscillations, and the ink was resistant to friction. The drying time of the ink is 4 seconds and this is an expected time for inkjet inks (Selim et al., 1997), the dry film weight is the most important parameter that determines the price of the ink. It is used to determine the amount of ink to be used in 1 m² area. Although there is no written rule, using less than 3 g of ink for an average of 1 m² is both cost-effective and covers the amount of ink that the paper can carry in consecutive prints. When the ink produced in this sense was examined, it was concluded that this requirement was met with 2.5 g/m². In addition, it has been determined that the ink has acid, alkali and nitro resistance with the tests performed. Thus, it has been determined that the ink can be used in detergent packages, cleaning materials as well as suitable for inks in different formulations that can be produced. Nitro resistance also shows that it is suitable for post-press applications such as cellophane after printing.

Conclusions

In this study, 1, 3, 6, 8-pyrene sulfonic acid tetrasodium fluorescent salt was synthesized as an ink colorant. The synthesis has been proven by ¹HNMR, and its optical properties have been proven by UV spectroscopy. Using this synthesized colorant, ink jet ink with hydroxy ethyl cellulose binder was produced and printed. When the prints were examined, it was determined that the ink was invisible under daylight and blue under UV light. It is also supported by the spectrophotometer with the same feature. When its printability properties are examined, it has been determined that it can be used industrially in good quality, compatible with post-printing applications and has light fastness that can be used in the open area for two years. It is thought that the obtained ink in line with the above-mentioned visual and printable features will provide secure information transfer and can be used in counterfeiting.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

- Arman Kandirmaz, E., Birtane, H., Beyler Cigil, A. & Ozcan, A. (2020) pH-controlled lavender oil encapsulation with ABA-type block copolymer and usage in paper coating. *Flavour and Fragrance Journal*. 35 (2), 174-181. Available from: doi: 10.1002/ffj.3549
- Bates, I., Džimbeg-Malčić, V. & Itrić, K. (2012) Optical deterioration of samples printed with basic Pantone inks. *Acta graphica: znanstveni časopis za tiskarstvo i grafičke komunikacije*. 23 (3-4), 79-90.
- Carreira, L., Agbezuge, L. & Gooray, A. (1995) Correlation between drying time and ink jet print quality parameters. In: *Proceedings of IS&T's Eleventh International Congress on Advances in Non-Impact Printing Technologies, 29 October – 3 November 1995, Hilton Head, South Carolina*. Springfield, Society for Imaging Science and Technology. pp. 334-337.
- Chakraborty, N., Chakraborty, A. & Das, S. (2018) A pyrene based fluorescent turn on chemosensor for detection of Cu²⁺ ions with antioxidant nature. *Journal of Luminescence*. 199, 302-309. Available from: doi: 10.1016/j.jlumin.2018.03.042
- Chang, K., Liu, Z., Chen, H., Sheng, L., Zhang, S. X. A., Chiu, D.T., Yin, S., Wu, C. & Qin, W. (2014) Conjugated polymer dots for ultra-stable full-color fluorescence patterning. *Small*. 10 (21), 4270-4275. Available from: doi: 10.1002/smll.201401436
- Chen, L., Hu, B., Zhang, J., Zhang, J., Huang, S., Ren, P., Zou, Y., Ding, F., Liu, X. & Li, H. (2019) A facile synthesis of 1, 3, 6, 8-pyrenesulfonic acid tetrasodium salt as a hydrosoluble fluorescent ink for anti-counterfeiting applications. *RSC Advances*. 9 (1), 476-481. Available from: doi: 10.1039/C8RA09106D
- Chen, Q., Li, X. & Chen, G. (2021) Vegetable oils based UV-luminescent ink for screen printed anti-counterfeiting marking. *Progress in Organic Coatings*. 151, 106009. Available from: doi: 10.1016/j.porgcoat.2020.106009
- Costa, A. L., Gomes, A. C., Pillinger, M., Goncalves, I. S. & Seixas de Melo, J. S. (2015) Controlling the fluorescence behavior of 1-pyrenesulfonate by cointercalation with a surfactant in a layered double hydroxide. *Langmuir*. 31 (16), 4769-4778. Available from: doi: 10.1021/acs.langmuir.5b00063
- Khan, R. I., Ramu, A. & Pitchumani, K. (2018) Design and one-pot synthesis of a novel pyrene based fluorescent sensor for selective "turn on", naked eye detection of Ni²⁺ ions, and live cell imaging. *Sensors and Actuators B: Chemical*. 266, 429-437. Available from: doi: 10.1016/j.snb.2018.03.137
- Leelajariyakul, S., Noguchi, H. & Kiatkamjornwong, S. (2008) Surface-modified and micro-encapsulated pigmented inks for ink jet printing on textile fabrics. *Progress in Organic Coatings*. 62 (2), 145-161. Available from: doi: 10.1016/j.porgcoat.2007.10.005
- Miskolczi, Z., Takahashi, Y., Kobayashi, N., Nakabayashi, S., Loukanov, A. & Biczók, L. (2018) Self-assembly of anionic pyrene derivatives with cationic surfactants bearing a tetradecyl chain. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 552, 161-168. Available from: doi: <https://doi.org/10.1016/j.colsurfa.2018.05.018>
- Pham, H. H., Gourevich, I., Oh, J. K., Jonkman, J. E. & Kumacheva, E. (2004) A multidye nanostructured material for optical data storage and security data encryption. *Advanced Materials*. 16 (6), 516-520. Available from: doi: 10.1002/adma.200306156
- Rodenburg, L., Floor, M., Lefeber, A., Cornelisse, J. & Lugtenburg, J. (1988) ¹H NMR and ¹³C NMR spectroscopy of pyrene dianions. *Recueil des Travaux Chimiques des Pays-Bas*. 107 (1), 1-8. Available from: doi: 10.1002/recl.19881070102
- Selim, M. S., Yesavage, V. F., Chebbi, R., Sung, S. H., Borch, J. & Olson, J. M. (1997) Drying of water-based inks on plain paper. *Journal of Imaging Science and Technology*. 41 (2), 152-158.
- Sonar, P., Soh, M. S., Cheng, Y. H., Henssler, J. T. & Sellinger, A. (2010) 1, 3, 6, 8-tetrasubstituted pyrenes: solution-processable materials for application in organic electronics. *Organic Letters*. 12 (15), 3292-3295. Available from: doi: 10.1021/ol1007179
- Song, Z., Lin, T., Lin, L., Lin, S., Fu, F., Wang, X. & Guo, L. (2016) Invisible security ink based on water-soluble graphitic carbon nitride quantum dots. *Angewandte Chemie International Edition*. 128 (8), 2823-2827. Available from: doi: 10.1002/ange.201510945
- Sun, L. W., Shi, H. Q., Li, W. N., Xiao, H. M., Fu, S. Y., Cao, X. Z. & Li, Z. X. (2012) Lanthanum-doped

ZnO quantum dots with greatly enhanced fluorescent quantum yield. *Journal of Materials Chemistry*. 22 (17), 8221-8227. Available from: doi: 10.1039/C2JM00040G

Yao, W., Tian, Q., Liu, J., Xue, Q., Li, M., Liu, L., Lu, Q. & Wu, W. (2017) Preparation and RGB upconversion optic properties of transparent anti-counterfeiting films. *Nanoscale*. 9 (41), 15982-15989. Available from: doi: 10.1039/C7NR05744J

You, M., Zhong, J., Hong, Y., Duan, Z., Lin, M. & Xu, F. (2015) Inkjet printing of upconversion nanoparticles for anti-counterfeit applications. *Nanoscale*. 7 (10), 4423-4431. Available from: doi: 10.1039/C4NR06944G



© 2024 Authors. Published by the University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license 3.0 Serbia (<http://creativecommons.org/licenses/by/3.0/rs/>).