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ARTICLE

A green approach to the synthesis of 2,3-diaminophenazine using a photocatalytic system of $CdFe_2O_4/TiO_2$ nanoparticles

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In recent years, the development of novel green chemistry routes for the synthesis of organic compounds has become very attractive to many research groups. Nanoparticles have been widely used because of their potential applications in catalysis, environmental remediation, electronic fields, biomedical, and industrial fields. In this article, a rapid, efficient, and simple approach was applied for the synthesis of 2,3-diaminophenazine using a new photocatalytic system of $CdFe_2O_4/TiO_2$ nanoparticles in water as a benign solvent. The structure of the synthesized $CdFe_2O_4/TiO_2$ nanoparticle was confirmed using different methods such as transmission electron microscope (TEM), X-ray diffraction (XRD), and magnetic measurements. It was found that the rate and yield of the photocatalytic synthesis of 2,3-diaminophenazine were improved using $CdFe_2O_4/TiO_2$ nanoparticles compared to other methods.

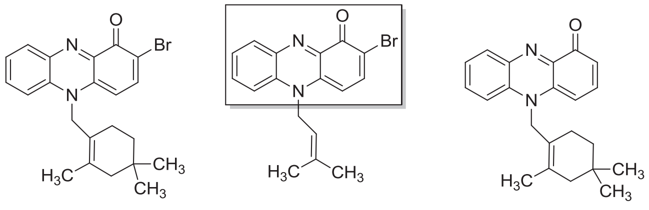
KEYWORDS

2,3-diaminophenazine, cadmium ferrite, green chemistry, nanoparticles, photocatalytic, titanium dioxide

1 | INTRODUCTION

Photocatalysis is one of the promising techniques that has important applications in many disciplines, that is, green energy, organic synthesis, and environment.[1–3] Selective photocatalytic reactions have attracted many scientists.[4–9] The photocatalytic selectivity enhancement was carried out via the photocatalyst modification, and changing the operational conditions. TiO_2-based photocatalysts have shown an excellent photocatalytic activity in various applications due to their good photochemical and chemical stability as well as superior light absorption.[10–14] In addition, magnetic nanoparticles (MNPs) are very interesting due to their multiple properties such as size effects, surface-to-volume ratio, magnetic separation, specificity, low toxicity, and the ability to control exposure and surface chemistry. Reducing and controlling exposure and hazard leads to low environmental risk. MNPs, in particular, nanozero-valent iron, magnetite, and maghemite have sparked potential applications in medicine, molecular biology, and remediation of polluted water.[15] Loading of Fe_2O_3 nanoparticles on TiO_2 may lead to better charge separation and enhanced photocatalytic activity of TiO_2.[16] Much attention has been paid to cadmium ferrite for its application in various fields[17,18] due to its strong absorption ability, better charge transport, and small band gap (1.97 ev).[19] Therefore, it was used for the removal and degradation of organic pollutants.[20–22] Cadmium iron (CdFe) nanoparticles were used as photocatalysts for oxidation and degradation of some dissolved organics in the presence of solar light irradiation and they exhibited good photocatalytic activity.[23] In addition, the photocatalytic activity of TiO_2 over different polymers and sodium alginate was studied previously.[24,25]

The importance of marine phenazines in medicinal chemistry is well recognized. In particular, phenazine derivatives have been used as potential cancer chemopreventive and anti-inflammatory agents.[26] Scheme 1 shows terpenoid-substituted phenazines (structure 1, N-substituted brominated



Brominated phenazine 1 **Brominated phenazine 2** **Lavanducyanin**

SCHEME 1 Some examples of bioactive marine phenazines

monoterpene phenazine; structure 2, N-substituted isoprenylated phenazine; and structure 3, lavanducyanin), which were isolated from the marine-derived Streptomyces sp. (strain CNS284).[27]

2,3-diaminophenazine (DAP) has received significant interest and particular attention in the last few decades due to its potential biological and physical applications. Many of such derivatives have shown wide biological uses. For example, they are used as anticancer drugs,[28,29] and in our recent work we investigated the antiproliferative activity of novel phenazinediamine derivatives against four cell lines,[30] antifungal,[31,32] antibacterial,[33] antimicrobial agents,[34] used as antibiotic,[35] antimycobacterium,[36,37] anthelmintics,[38–40], and antioxidants and stabilizers.[41] They are also used on a large scale as eye drops for cataract[42] and as inhibitors of advanced glycation.[43]

In addition to the previous biological applications of phenazine derivatives, many investigations of the fluorescence of 2,3-diaminophenazine have typically focused on its use in the development of new analytical applications and detection techniques.[44–47] The synthesis of 2,3-diaminophenazines is very attractive to many research groups who are investigating environmentally friendly routes to overcome the preparation problems such as low yields. 2,3-Diaminophenazine **1** was prepared by catalytic oxidation of o-phenylenediamine **2** by various oxidizing agents such as ferric chloride,[48] silver oxide, lead(IV) oxide, cupric chloride, copper(II)hydroxide,[44] cobalt perchlorate,[49] dinuclear cobalt(II)–OBISDIEN dioxygen complex,[50] and ferric sulfate.[51]

Moreover, The enzyme (biochemical)-catalyzed oxidation of OP was reported as an alternative way[52] to yield DAP in a 42% yield using the horseradish peroxidase (HRP)-catalyzed oxidation. Similar to HRP, laccase, a copper-containing polyphenol oxidase dominantly produced in microorganisms and plants, also has the ability to achieve the catalytic oxidation. When an ethanolic solution of *o*-phenylenediamine was exposed to Ultraviolet (UV) light (275.3 nm) while air was bubbled through it, it formed 2,3-diaminophenazine.[53,54]

In continuation of our efforts to develop and discover new efficient classes of bioactive compounds and green synthetic approaches,[55,56] we will investigate for the first time the use of environmental nanotechnology to overcome preparation limitations using a simple, cost-effective catalyst such as $CdFe_2O_4/TiO_2$ nanocomposites for the photocatalytic synthesis of 2,3-diaminophenazine.

2 | EXPERIMENTAL

All chemicals employed were of analytical grade and supplied by BDH Company. TiO_2 from Aldrich (anatase) was used. Melting points were determined by Electrothermal Engineering LTD apparatus in open capillary tubes and are uncorrected.

Analytical thin-layer chromatography was performed with 0.25 mm commercial silica gel plates (EMD, Silica Gel $60F_{254}$). TLC plates were visualized by UV fluorescence at 254 nm.

X-ray diffraction was performed using a Bruker diffractometer (Bruker D 8 advance target). The nanostructure of the samples was examined using a JEOL-2100 high-resolution transmission electron microscope (HRTEM) with an accelerating voltage of up to 200 kV. The magnetic properties were measured using a vibrating sample magnetometer (VSM; 9600-1 LDJ).

For GC–MS analysis, 1 L of the sample was extracted with a mixture of dichloromethane, hexane, and ether at pH 2 and 11. The extracts were diluted with dichloromethane and analyzed by gas chromatography using a Thermo scientific, Trace GC Ultra/ISQ single Quadrupole MS, TG5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm). The GC oven was heated from 40 to 280°C at a rate of 5°C/min. The analysis was carried out in the splitless mode. Helium was used as a carrier gas. Mass spectra were recorded at EI 70 eV, and Helium was used as a carrier gas. The identification of compounds was performed based on the NIST and Willy library data of the GC–MS system.

2.1 | Preparation of $CdFe_2O_4$

Cadmium ferrites ($CdFe_2O_4$) were prepared using the wet chemical coprecipitation route. The nitrates of cadmium and iron were dissolved in 1 L of distilled water at the designated molar ratio (Fe/Cd = 2). An aqueous solution of 1 M Na_2CO_3 was used as the precipitating agent. The metal nitrate and the Na_2CO_3 solutions were added dropwise from three separate burettes into a reaction vessel containing 1 L of distilled water under mechanical stirring. The coprecipitation method was carried out by taking 50 mL of ferric nitrate and 50 mL of cadmium nitrate followed by dropwise addition of 50 mL of Na_2CO_3 solution until complete coprecipitation procedure of all mixed carbonates. The rate of addition was controlled to maintain a constant pH = 8 during the coprecipitation process. The coprecipitation method was thermostated at 70°C. The precipitate was carefully washed until being free from NO_3^- and Na^+ ions. It was then filtered, dried at 100°C overnight, and then calcined at 600°C for 5 hr to achieve transformation into the spinel phase.

2.2 | Preparation of $CdFe_2O_4/TiO_2$ nanocomposites

The TiO_2 powder (1 g) and $CdFe_2O_4$ (0.3 g) were mixed and ground together and dispersed in 25 mL of ethanol and 50 mL of deionized water. The mixture was then sonicated for 1 hr in air at room temperature. The obtained powders after filtration were dried at 105°C and then ground into very fine size. The ground powders were washed with distilled water to eliminate the TiO_2 particles loosely attached to the prepared samples and finally dried at 100°C.

2.3 | Characterization

X-ray powder diffraction of various investigated samples calcined at 600°C was determined using a Bruker diffractometer (Bruker D 8 advance target). The patterns were run with CuKα with a second monochromator ($\lambda = 1.5405$ Å) at 40 kV and 40 mA. The scanning rate was 8° and 0.8° in 2θ min^{-1} for phase identification and line broadening profile analysis, respectively. The crystallite size of the phases present in pure and various La_2O_3-treated solids was determined using the Scherrer Equation [57]:

$$d = K\lambda/\beta_{1/2} \cos\theta,$$

where d is the mean crystalline diameter, λ is the X-ray wavelength, K is the Scherrer constant (0.89), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the main diffraction peaks of the investigated phases, in radian, and θ is the diffraction angle.

The nanostructure of the samples was examined using very dilute suspensions in water with the aid of a JEOL-2100 HRTEM with an accelerating voltage up to 200 kV. The microscopy probes of the sample were prepared by adding a small drop of the water dispersions onto a lacey carbon film-coated copper grid and allowed to dry initially in the air then by applying high vacuum.

The magnetic properties of the investigated solids were measured at room temperature using a VSM (9600-1 LDJ) in a maximum applied field of 15 kOe. From the obtained hysteresis loops, the saturation magnetization (*M*s), remanence magnetization (*Mr*), and coercivity (*Hc*) were determined.

2.4 | Photocatalytic reactions

2.4.1 | Photooxidation of o-phenylenediamine without catalyst (method A)

In a typical synthesis, o-phenylenediamine (15 mg) in distilled water (100 mL), the solution was placed under a UV light source (High-pressure mercury lamp, 125 W) and irradiated for 4 hr at room temperature. Ethyl acetate (5 mL) was added, and the organic material was extracted. The organic phase was dried, and the solvent was evaporated under reduced pressure to give the product as a brown powder. Yield, 25%. m.p. 260–268°C, MS (EI) *m/z*: 210.6 (M^+). All the spectroscopic and physical data were identical to a commercial sample from Sigma Aldrich.

2.4.2 | Photocatalytic oxidation of o-phenylenediamine using TiO_2 (method B)

Titanium dioxide (10 mg) was added to a solution of o-phenylenediamine (15 mg) in distilled water (100 mL), and the reaction mixture was stirred for 15 min in the dark. After that, the mixture was placed under a UV light source (150 W) and irradiated for 4 hr at room temperature. Ethyl acetate was added, and the organic material was extracted. The organic phase was dried and the solvent was evaporated under reduced pressure to give the product as a brown powder. Yield, 50%. m.p. 260–268°C, MS (EI) *m/z*: 210.6 (M^+).

2.4.3 | Photocatalytic oxidation of o-phenylenediamine using the $CdFe_2O_4/TiO_2$ composite (method C)

The $CdFe_2O_4/TiO_2$ composite (10 mg) and o-phenylenediamine (15 mg) were dissolved in distilled water (100 mL). The mixture was then placed under a UV light source (High-pressure mercury lamp, 125 W) and irradiated for 4 hr at room temperature. Ethyl acetate was added and the organic material was extracted. The organic phase was dried, and the solvent was evaporated under reduced pressure to give the product as a brown powder. Yield, 65%. m.p. 260–268°C, MS (EI) *m/z*: 210.6 (M^+).

3 | RESULTS AND DISCUSSION

3.1 | X-ray investigation of various solids

Figure 1 shows the x-ray diffraction patterns of the synthesized pure sample and composite ($CdFe_2O_4/TiO_2$). Sharpe

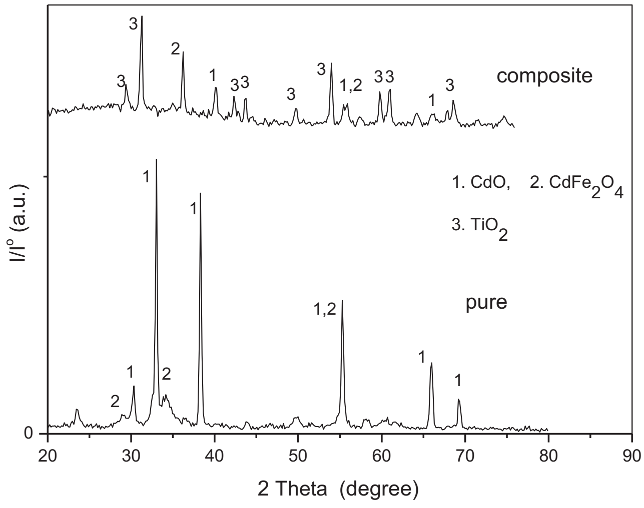


FIGURE 1 XRD diffractograms of pure $CdFe_2O_4$ and the $CdFe_2O_4$ /TiO_2 nanocomposite

and well-defined peaks are obtained for both samples. The role of TiO_2-treatment in $CdFe_2O_4$ formation could be discussed as; a portion of TiO_2 might dissolve in the cadmium oxide matrix. The dissolution process could be simplified according to KrÖger notations [58]:

$$Ti^{4+} + Cd^{2+} \rightarrow Ti\left(Cd^{2+}\right) + \text{A.V.} \qquad (1)$$

where, $Ti(Cd^{2+})$ is the titanium ion located in the position of Cd^{2+} and "A.V." is created anionic vacancies. These vacancies facilitate migration of reacting cations that is, increasing the mobility of divalent cadmium cations taking part in cadmium ferrite formation. This might be tentatively attributed to the role of TiO_2 in accelerating $CdFe_2O_4$ formation. This would be discussed in the magnetic section in this article.

3.2 | TEM studies

It could be shown from the transmission electron microscope (TEM) images in Figure 2 that the $CdFe_2O_4/TiO_2$ composite possesses an almost homogeneous structure; $CdFe_2O_4$ nanoparticles have a particle size of 65–98 nm and TiO_2 nanoparticles have a particle size of 35–55 nm. No free $CdFe_2O_4$ particles are observed in the as-synthesized sample.

3.3 | Magnetic properties

Figure 3 shows the magnetic moment of bare TiO_2 and $CdFe_2O_4/TiO_2$ composites. From this figure, we can deduce that TiO_2 decreases the magnetic properties of $CdFe_2O_4$ from 2.227 to 1.785 emu/g. However, the composite still has good magnetic properties, which is considered as the promising catalyst that could be easily removed from the reaction medium. The pattern of decrease of the magnetic properties due to the decrease of iron oxide that reacts with cadmium oxide is as shown in the X-ray diffraction (XRD) section (Figure 1).

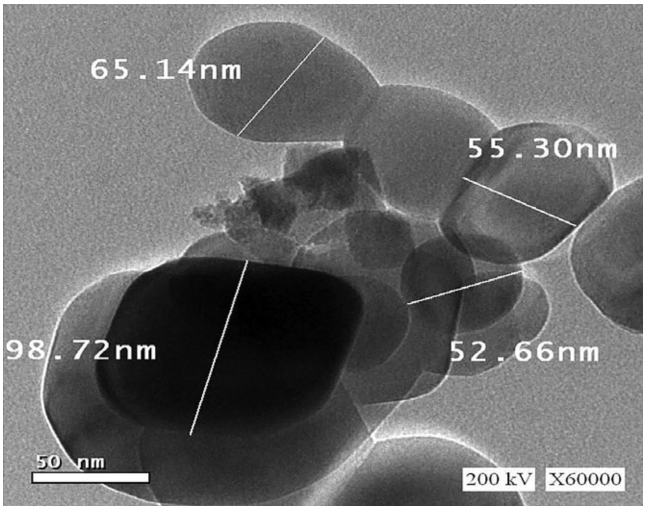


FIGURE 2 TEM image of the $CdFe_2O_4/TiO_2$ composite

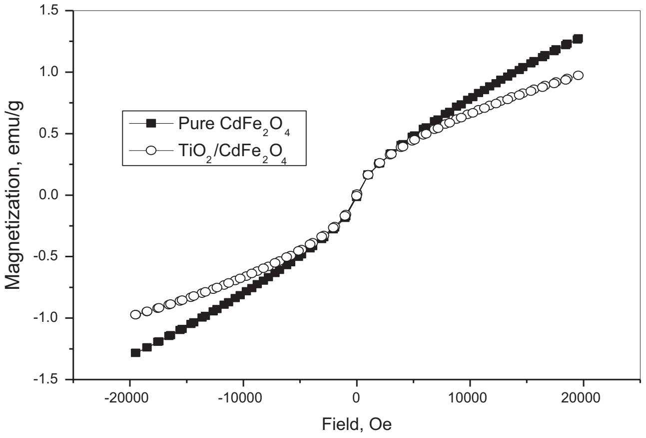


FIGURE 3 Magnetic measurements of pure $CdFe_2O_4$ and $CdFe_2O_4/TiO_2$

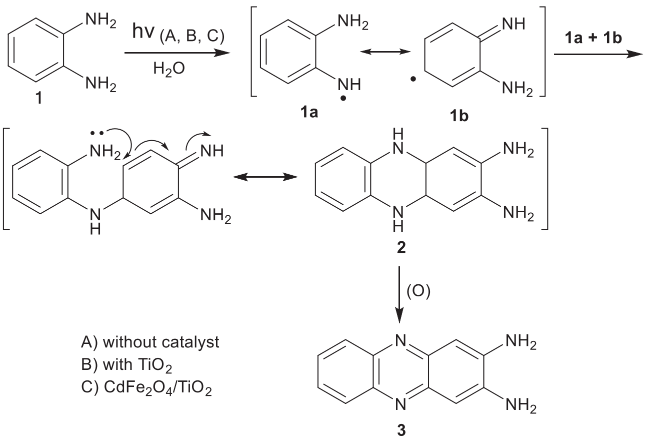
3.4 | Photocatalytic activity

Heterogeneous photocatalysts obtained using TiO_2 and its nanocomposites have attracted significant interests in green chemical processes, where scientists seek higher photocatalytic efficiency and selectivity under mild and environmentally friendly conditions. Excitation of TiO_2 particles by UV irradiation at wavelengths corresponding to the band gap value promotes electrons at the conduction band leaving positive holes at the valence band. If electrons and holes could reach the surface of the semiconductor before recombination takes place, they may induce redox processes of organic substrates. In the absence of O_2, conduction band electrons are expected to reduce the organic substrates while the powerful oxidizing properties of the photogenerated holes should lead to the oxidation of the organic substrate with the possibility of involvement of adsorbed $OH^{\cdot}$ radicals [59].

3.5 | Photocatalytic synthesis of 2,3-diaminophenazine

Three methods have been investigated for achieving the photocatalytic conversion of o-phenylenediamine, the first method (method A) involves the photooxidation in the absence of any catalyst, so irradiation of water solution of o-phenylenediamine at room temperature gave 2,3-diaminophenazine in 25% yield. As a trial to enhance the yield of conversion, TiO_2 was used as a catalyst (method B). Therefore, after 4 hours of irradiation in the presence of TiO_2, the target product was formed in 50% yield. The third method (method C) involves the use of a composite $CdFe_2O_4/TiO_2$, which enhanced the yield to be about 65%, and at the same time, showed the advantage of the possibility to recycle the catalyst thanks to its magnetic properties. The target product was characterized using GC-mass spectrometry.

The proposed pathway in Scheme 2 was suggested to account for the photoconversion of o-phenylenediamine to 2,3-diaminophenazine, the first step involves the photocatalytic oxidation of o-phenylenediamine by $TiO_2(h^+)$ to form



SCHEME 2 Proposed pathway for the photocatalytic conversion of o-phenylenediamine to 2,3-diaminophenazine

the radicals (**1a**, **1b**) and H^+. Reduction of H^+ using TiO_2 (e^-) forms H_2. While recombination of radicals (**1a**, **1b**) forms the intermediate **2**. Attacking by the lone pair of electrons of the amino group and hydrogen migration afford **3**, which upon oxidation forms 2,3-diaminophenazine as the end product.

$TiO_2(h^+) + 2Ar\text{-}(NH_2)_2 = 2Ar\text{-}(NH_2)\text{-}NH\cdot + 2H^+ + TiO_2$

$TiO_2\ (e-) + 2H^+ = H_2$ [60]

The significant enhancement in photoactivity is attributed to the synergism between $CdFe_2O_4$ and TiO_2, that is, effective charge transfer from TiO_2 to $CdFe_2O_4$ and the suppression of electron/hole pair recombination [61].

$CdFe_2O_4$ also plays an important role in charge separation and in improving the electron–hole separation of TiO_2 due to the synergetic effect between TiO_2 and $CdFe_2O_4$. It was considered that the O-2p orbital could act as a valence band and the Fe-3d orbital could act as a conduction band of $CdFe_2O_4$. As a result of electron excitation from the O-2p level into the Fe-3d level, absorption of $CdFe_2O_4$ within the UV irradiation is possible. This makes it feasible to increase the electron transfer rate within the photocatalytic system. Therefore, in the presence of cadmium ferrite, an improved photocatalytic capability was achieved [62,63].

4 | CONCLUSIONS

In this work, green synthesis of 2,3-diaminophenazine using a photocatalytic system of $CdFe_2O_4/TiO_2$ nanocomposites was reported. The prepared $CdFe_2O_4/TiO_2$ was fully characterized using TEM, XRD, and Magnetic measurements. The characterization results showed that $CdFe_2O_4$ nanoparticles have a particle size of 65–98 nm and TiO_2 nanoparticles have a particle size of 35-55 nm. The $CdFe_2O_4/TiO_2$ nanocomposites have good magnetic properties and a homogenous surface. The prepared nanocomposites showed good photocatalytic activity toward the green photocatalytic synthesis of 2,3-diaminophenazine using water as a benign solvent in the presence of UV irradiation.

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REFERENCES

[1] J. Kou, R. S. Varma, *Chem. Sus. Chem.* **2012**, *5*, 2435.
[2] D. Scanlon, C. Dunnill, J. Buckeridge, S. Shevlin, A. Logsdail, S. Woodley, C. A. Catlow, M. Powell, G. Palgrave, *Nat. Mater.* **2013**, *12*, 798.
[3] T. Simon, N. Bouchonville, M. Berr, A. Vaneski, A. Adrovic, D. Volbers, R. Wyrwich, M. Doeblinger, A. Susha, A. Rogach, *Nat. Mater.* **2014**, *13*, 1013.
[4] J. Kou, R. Varma, *Nanoscale.* **2013**, *5*, 8675.
[5] Y. Shiraishi, N. Saito, T. Hirai, *J. Am. Chem. Soc.* **2005**, *127*, 12820.
[6] S. Ikeda, H. I. Kobayashi, T. Harada, T. Torimoto, B. Ohtani, M. Matsumura, *Phys. Chem. Chem. Phys.* **2007**, *9*, 6319.
[7] S. Ikeda, Y. Ikoma, H. Kobayashi, T. Harada, T. Torimoto, B. Ohtani, M. Matsumura, *Chem. Commun.* **2007**, *36*, 3753.
[8] K. Inumaru, M. Yasui, T. Kasahara, K. Yamaguchi, A. Yasuda, S. Yamanaka, *J. Mater. Chem.* **2011**, *21*, 12117.
[9] T. Ruberu, N. Nelson, I. Slowing, J. Vela, *J. Phys. Chem. Lett.* **2012**, *3*, 2798.
[10] W. Fang, X. Gong, H. Yang, *J. Phys. Chem. Lett.* **2011**, *2*, 725.
[11] T. Tachikawa, S. Yamashita, T. Majima, *J. Am. Chem. Soc.* **2011**, *133*, 7197.
[12] Y. Ide, R. Ogino, M. Sadakane, T. Sano, *Chem. Cat. Chem.* **2013**, *5*, 766.
[13] A. Syafiuddin, T. Hadibarata, N. F. Zon, Salmiati, *J. Chin. Chem. Soc.* **2017**, *64*, 1333. https://doi.org/10.1002/jccs.201700136.
[14] M. Chen, C. Chen, R. Wu, C. Lu, *J. Chin. Chem. Soc.* **2013**, *60*, 380. https://doi.org/10.1002/jccs.201200027.
[15] J. Kudr, Y. Haddad, L. Richtera, Z. Heger, M. Cernak, V. Adam, O. Zitka, *Nanomaterials* **2017**, *7*, 243.
[16] S. Moniz, S. Shevlin, X. An, Z. Guo, J. Tang, *Chem. Eur. J.* **2014**, *20*, 15571.
[17] O. Silva, P. Morais, *J. Magn. Magn. Mater.* **2005**, *289*, 136.
[18] M. Yokoyama, E. Ohta, T. Sato, *J. Magn. Magn. Mater.* **1998**, *183*, 173.
[19] F. Miao, Z. Deng, X. Lv, G. Gu, S. Wan, X. Fang, Q. Zhang, S. Yin, *Solid State Commun.* **2010**, *150*, 2036.
[20] W. Shi, X. Liu, T. Zhang, Q. Wang, L. Zhang, *RSC Adv.* **2015**, *5*, 51027.
[21] V. Vasanthi, A. Shanmugavani, C. Sanjeeviraja, R. Kalai Selvan, *J. Magn. Magn. Mater.* **2012**, *324*, 2100.
[22] T. Lai, C. Lee, K. Wu, Y. Shu, C. Wang, *Appl. Catal. B* **2006**, *68*, 147.
[23] S. B. Patil, H. S. Bhojya Naik, G. Nagaraju, Y. Shiralgi, *Eur. Phys. J. Plus* **2018**, *133*, 229.
[24] A. Ghanem, A. Badawy, N. Ismail, Z. Rayn, M. Abdel Rehim, A. Rabia, *Appl. Catal. A: Gen.* **2014**, *472*, 191.
[25] M. Abdel Rehim, M. El-Samahy, A. Badawy, M. Mohram, *Carbohydr. Polym.* **2016**, *148*, 194.
[26] M. Makgatho, R. Anderson, J. O'Sullivan, T. Egan, J. Freese, Cornelius, N. C. Rensburg, *Drug Dev. Res.* **2000**, *50*, 195.
[27] T. Kondratyuk, E. Park, R. Yu, R. Breemen, R. Asolkar, B. Murphy, W. Fenical, J. Pezzuto, *Mar. Drugs* **2012**, *10*, 451.
[28] G. Rewcastle, W. Denny, B. Baguley, *J. Med. Chem.* **1987**, *30*, 843.
[29] X. Gao, Y. Lu, Y. Xing, Y. Ma, J. Lu, W. Bao, Y. Wang, T. Xi, *Microbiol. Res.* **2012**, *167*, 616.
[30] A. Mahran, S. Ragab, A. Hashem, M. Ali, A. Nada, *Eur. J. Med. Chem.* **2015**, *90*, 568.
[31] M. Wang, H. Xu, S. Yu, Q. Feng, S. Wang, Z. Li, *J. Agric. Food Chem.* **2010**, *58*, 3651.
[32] H. Liu, Y. He, H. Jiang, H. Peng, X. Huang, X. Zhang, L. Thomashow, Y. Xu, *Curr. Microbiol.* **2007**, *54*, 302.

[33] A. Hernandez, A. Kappler, D. Newman, *Appl. Environ. Microbiol.* **2004**, *70*, 921.

[34] H. Hussain, S. Specht, S. Sarite, M. Saeftel, A. Hoerauf, B. Schulz, K. Kroh, *J. Med. Chem.* **2011**, *54*, 4913.

[35] T. Siunova, V. Kochetkov, S. Validov, N. Suzina, A. Boronin, *Microbiology* **2002**, *71*, 670.

[36] B. Zeis, R. Anderson, J. O'sullivan, *Antimicrob. Agents Chemother.* **1987**, *31*, 789.

[37] S. Franzblau, J. O'sullivan, W. Gillis, *Antimicrob. Agents Chemother.* **1988**, *32*, 1583.

[38] V. Zikan, J. Sluka, J. Danek, CS 258596 (Cl. C07D487/04, 15 Mar 1989, Appl, 87/1,304. 26 Feb **1987** 4p).

[39] V. Zikan, J. Sluka, J. Danek, CS 254605 (Cl. C07D241/46, 15 Sep 1988, Appl, 86/3,357. May 8, **1986** 3p).

[40] V. Zikan, J. Sluka, CS 254604 (Cl. C07D241/46, 15 Sep 1988, Appl, 86/3,356. May 8, **1986**; 2p).

[41] J. Rotschova, L. Taimer, J. Pospisil, *J. Chromatogr.* **1981**, *216*, 251.

[42] C. Tie-Min, F. Zhao-Xia, C. Ji-Qiao, C. Pei-ching, J. Hsueh Yuan, *Hsueh-Pao* **1980**, *12*, 262.

[43] E. Roufail, T. Soulis, E. Boel, M. Cooper, S. Rees, *Diabetologia* **1998**, *41*, 1419.

[44] H. Zuyun, H. Huang, R. Cai, Y. Zeng, *Anal. Chim. Acta* **1998**, *374*, 99.

[45] R. X. Cai, *Talanta* **2000**, *51*, 179.

[46] K. Zhang, R. Cai, D. Chen, L. Mao, *Anal. Chim. Acta.* **2000**, *413*, 109.

[47] R. Doyle, P. Kruger, P. Mackie, M. Nieuwenhuyzen, *ActaCrystallogr. C* **2001**, *57*, 104.

[48] H. Mager, W. Berends, *Rec. Trav. Chem.* **1957**, *76*, 28.

[49] G. Crank, M. Makin, *J. Heterocyclic Chem.* **1989**, *26*, 1163.

[50] N. Rosso, B. Szpoganicz, A. Martell, *Inorg. Chim. Acta* **1999**, *287*, 193.

[51] M. Furnica, *Bull. Inst. Politech. Iasi* **1978**, *24*, 35.

[52] P. J. Tarcha, V. Chu, D. Whittern, *Anal Biochem.* **1987**, *165*, 230.

[53] V. Mekler, O. Belonogova, V. Nikulin, *J. Photochem. Photobiol. A: Chem.* **1995**, *87*, 243.

[54] V. Mekler, S. Bystryak, *Photochem. Photobiol. A* **1992**, *5*, 391.

[55] M. Mady, G. Awad, K. Jorgensen, *Eur. J. Med. Chem.* **2014**, *84*, 433.

[56] N. El-Rahman, T. Saleh, M. Mady, *Ultrason. Sonochem.* **2009**, *16*, 70.

[57] B. D. Cullity, *Publishing Cos*, 2nd ed., Addison-Wesley, Reading, MA **1978**, p. 102.

[58] F. Kröger, *Chemistry of Imperfect Crystals*, North-Holland, Amsterdam **1964**.

[59] P. Paola, C. Minero, M. Vincenti, E. Pelizzetti, *Catal. Today* **1997**, *39*, 187.

[60] D. Friedmann, A. Hakki, H. Kim, W. Choi, D. Bahnemann, *Green Chem.* **2016**, *18*, 5391.

[61] S. Kang, B. Kwak, M. Park, K. Jeong, S. Park, M. Kang, *Bull. Korean Chem. Soc.* **2014**, *35*, 2813.

[62] S. Sagadevan, K. Pal, Z. Chowdhury, M. Hoque, *Mater. Res. Express* **2017**, *4*, 075025.

[63] S. Xu, D. Feng, W. Shangguan, *J. Phys. Chem. C* **2009**, *113*, 2463.

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