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Crystal structure of AgSCN coordination polymers for sensing of iron (III) ions, Nitrobenzene and photocatalytic activity under ultrasonic irradiation

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Abstract

Single crystals of AgSCN supramolecular coordination polymer, SCP1 and the nanosized particles of AgSCN, **2**, are synthesized by self-assembly and ultrasonic radiation methods, respectively. The structure comprises of the simple AgSCN molecule fabricated by a tetrahedral Ag atom and one thiocyanate group. The SCN ligand connects four Ag atoms via μ_3 -S and one nitrogen atom. Two silver atoms and two sulfur atoms form rhombic mini-cycle (Ag_2S_2) motif exhibiting argentophilic interaction. The structure of SCP1 extends three-dimensionally via coordinate bonds creating different fused polygons. The chemical structure and morphology of nanosized **2** are characterized by powder X-ray diffraction and transmission electron microscopy (TEM) and spectroscopic methods. The heterogeneous catalytic and photo-catalytic activity of nanosized **2** exhibit very efficient catalytic activity towards degradation of Acid Blue-92 and Eosin-Y dyes within very short times under UV-light or ultrasonic radiation. The good limit of detection and the high quenching efficiency of SCP1 towards selective quantitative determination of nitrobenzene (NB) and Fe^{3+} ions support its behavior as an efficient luminescent sensor.

Keywords: Nanosized AgSCN, Crystal structure, Luminescent sensor, Photocatalytic degradation; Acid Blue 92, Eosin-Y, Nitrobenzene.

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1. Introduction

A significant attention was paid in recent years for supramolecular coordination polymers (SCPs) and consequently metal organic frameworks (MOFs) as polymorphic and multipurpose materials [1]. Such materials are assembled using different techniques giving variable and limitless structures with high surface area, tunable optical properties, perpetual porosity and high adsorption affinity [2, 3]. SCPs showed a great efficiency as heterogeneous catalysts [4], chemical sensors [5, 6], nanofluid additives [7], as well as their effective role in drug delivery [8], storage and separation [1, 9]. The high porous nature and surface area enhance the catalytic ability of SCPs. As many chemical processes, the heterogeneous catalysis is one of the main solutions of our developed society [10]. Due to the high efficiency, low cost, and lack of secondary environmental pollution, the photocatalysis has attracted high interest. The discharge of industrial dye polluted wastewater effluents into aquatic sources causes severe problems to human health and impact the aquatic environment. In order to minimize the harmful effects of toxic dyes on humans and the environment, SCPs were used as heterogeneous catalysts for degrade such dyes [5]. Pollution of surface and ground water with heavy metal ions as Fe(III) ions can cause damage and disease to humans or other organisms [11]. Sensitive and selective detection of these ions are of biological, industrial and environmental interest [12]. SCPs are also considered as desirable chemical sensor materials for the detection of small molecular species such as ions in water system [13]. The short response time and high selectivity are the main advantages of luminescent SCPs as chemical sensors [14, 15]. Silver (I) based SCPs have attracted great concern due to their aesthetic architectures and promising applications where, Ag(I) has a tendency to form Ag...Ag interaction, which has greatly enriched Ag-SCPs motifs [16]. On the other hand, the thiocyanate compounds were known as good semiconductors because they easily adsorb

many organic and inorganic substances that this property is essential for photocatalysts and dye-sensitized photovoltaic systems [17]. Here, the synthesis and characterization of single crystals (AgSCN) SCP1 and the nanosized particles 2, will be discussed respectively, by self-assembly and sonochemical methods as well as their applications in photodegradation of toxic organic dyes such as Acid Blue 92 (AB-92), [scheme 1](#) and Eosin-Y (EO-Y), [scheme 2](#), as a model pollutants. Additionally, the luminescence behavior of SCP1 is investigated to detect its ability as sensor for selective determination of nitrobenzene and metal ions.

2. Experimental

2.1. Materials and measurements

All utilized organic solvents and reagents in this study were purchased from Sigma-Aldrich with excessive purity available and were used as received. The analytical and physical measurements for the structural characterization were similar to those used in our previous works [18, 19].

2.2. Synthesis of silver thiocyanate single crystals; $^3\infty$ [AgSCN], SCP1

At ambient conditions, three solutions of AgNO₃ [1.0 mmol in 15 mL H₂O], KSCN [0.2 mmol in 10 mL H₂O], and ethyl iso-nicotinate (EIN) ligand [0.4 mmol in 20 mL of CH₃CN and H₂O (1:1)] were mixed, stirred for 30 min and kept enclosed for two weeks to obtain EIN free colorless prismatic single crystals of silver thiocyanate [AgSCN], SCP1 by self-assembly method. The crystals were filtered off, washed with CH₃CN/H₂O (1:1) solvents and then were dried. IR spectrum of SCP1 as KBr pellet exhibits bands at 3476br, 3097w, 1732s, 1620s, 1588s, 1555s, 1451s 1387 m, 1267 m, 751s, 647 m, 546 m, 521w, 492w cm⁻¹, [Fig. S1](#).

2.3. Synthesis of nanosized 2 silver thiocyanate

At the same amounts and conditions of SCP1 preparation and through ultrasonic bath, the mixture of the ternary adducts was subjected to ultrasonic radiation for 60 min at 30 °C with a distinct power of 70 W to synthesize nanosized particles **2**. The resultant precipitate was centrifuged, washed with 20 mL H₂O and then was dried where about 68% of nanosized **2** was obtained. The elemental analysis data of AgSCN nanosized **2** (M.W. = 156.95 g/mol) are Anal. Calculated: C, 7.65%; N, 8.92%; S, 20.42%; Ag, 68.72%, Found: C, 7.71%; N, 8.852%; S, 20.65%; Ag, 68.64%. IR spectrum of SCP1 as KBr pellet exhibits bands at 3478br, 3098w, 1733s, 1622s, 1589s, 1557s, 1452s 1387 m, 1268 m, 752s, 648 m, 546 m, 521w, 493w cm⁻¹, [Fig. S1](#).

2.4. Photocatalytic activity measurements of the nanosized **2**

The photocatalytic activity of the nanosized **2** for degradation of both Acid Blue-92 (AB-92) dye ($\lambda = 560$ nm) and Eosin-Y (EO-Y) dye ($\lambda = 514$ nm), [Schemes S1 and S2](#), were tested under ambient conditions (AC), UV-light radiation using a 300 W high pressure mercury lamp and ultrasonic radiation through ultrasonic bath 70 W. Typically, the photocatalytic experiments were carried out by mixing 25 mg of AgSCN nanosized **2** as a heterogeneous catalyst with 50 mL aqueous dye solution of AB-92 (5×10^{-5} M) or EO-Y (2.5×10^{-4} M)] in presence of (0.1 M) H₂O₂. The solution was then stirred magnetically in dark chamber for one hour till attains equilibrium between desorption and adsorption. During each process and at definite time, about 5 mL of solution was continuously taken, filtered off and was analyzing using UV–visible spectrometer. The same procedures were used in control experiments without using any catalyst. Also, the photocatalytic activity of **2** in presence of ammonium oxalate (AO), benzoquinone (BQ), and isopropanol (IPA) were investigated under UV-light irradiation. The catalytic degradation efficiency ($D\%$) was calculated using [Eq. 1](#),

$$D\% = \frac{C}{C_0} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad (1)$$

Where A_0 and A_t are the absorbance of AB-92 or EO-Y dyes at zero time and at time t (min).

2.5 The luminescence and sensing properties of SCP1

A certain amount (5 mg) of SCP1 as fine powder was suspended in 10 mL of some organic solvents which include DMSO, MeOH, CHCl_3 , CH_2Cl_2 , THF, EtOH, IPA, CH_3CN , DMF, CCl_4 , acetone and nitrobenzene (NB). Then the fluorescence spectra of the suspensions formed by ultrasonic irradiation were measured. Also, the same procedure was followed up to investigate the luminescence behavior of SCP1 to selectively detect metal ions, $M = \text{K}^+, \text{Na}^+, \text{Ba}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}, \text{Cd}^{2+}, \text{Fe}^{2+}, \text{Pb}^{2+}$ and Fe^{3+} by adding 5 mg of SCP1 in CH_3CN solution which contains a constant amount of $M(\text{NO}_3)_n$ (1×10^{-3} mol. L^{-1}). Then the suspension was put in ultrasonic for 10 min and the fluorescent intensity was measured at ambient conditions upon excitation at 360 nm [20].

2.6 X-ray crystallography of single crystal of SCP1

Crystal structure determination of SCP1 had been measured using a Kappa CCd Enraf Nonius FR 90 four circle goniometer with graphite monochromatic MoK α radiation $\{[\lambda \text{ MoK}\alpha] = 0.71073 \text{ \AA}\}$ at $25 \pm 2^\circ \text{C}$. The methods used to solve the structure of **1** are performed as previously reported Rabie [4]. Structure solution, refinement by full-matrix least-squares techniques on F^2 and data out-put have been completed using SHELX-97 and SIR92 programs [21]. For structure visualizations, Mercury 3.8 software was applied. Crystal data and structure refinement parameters of SCP **1** are listed in Table 1.

3 Results and Discussion

3.1 X-Ray crystal structure of $^3\infty[\text{AgSCN}]$, SCP1

Lindqvist [22] had early studied the crystal structure of AgSCN in the space group $C1/c$. The structure unit is an endless chain formed by covalent bonds from a silver atom to N- and S-atoms of two thiocyanate groups creating a zigzag shape with bent structure. On the other hand, the crystal structure was recently refined by H.-L. Zhu indicating the formation of 3D- structure via Ag—S bonds and weak Ag---Ag interaction and each Ag atom has a T-shape coordination environment [23]. Ag atoms, two thiocyanate ligands and four S atoms of additional SCN- groups form the fourteen-membered rings, which had been recognized as an essential unit of the AgSCN complex [23]. In the present discussion, we present a new overlook for the pretty crystal structure of the 3D-coordination polymer AgSCN; SCP1.

One crystal X-ray diffraction analysis of **1** confirms the monoclinic crystal system with the space group $C12/c1$ and $Z=8$, Table 1. The asymmetric unit of SCP1 consists of the simple AgSCN molecule fabricated by one Ag atom and one thiocyanate group, as shown in Fig. 1a. The packing structure shows tetrahedral (T-4) coordination geometry around the Ag1 atom which is connected to three μ_3 -S2 atoms and one nitrogen end of the thiocyanate ligand which seems to be quite different than the long-recognized coordination environment of T-shape fashion [23], as can be seen in Figs. 1b,c. Thus, the SCN ligand connects four Ag atoms via μ_3 -S and one nitrogen atom. Three different Ag1- μ_3 -S2 bond lengths are observed in the structure of **1** [2.4749(13), 2.8415(16) and 2.9973(17) Å], Table S1. The last two Ag1- μ_3 -S2 bond lengths are obviously longer, while the first one is shorter than even present in molecular AgSCN (2.648 Å) [24] and those of the prototype compounds (2.6118- 2.6543 Å) [25, 26]. Also, the Ag1-N4 bond length exhibits shorter distance [2.156(4) Å] while the S2-C3 and C3-N4 bond lengths [1.660(4) and 1.166(6)], respectively, are in the range of prototype compounds.

The angles around the silver atom; 107.28(4), 97.07(3), 163.27(11) and 92.13(12) Å, support the formation of distorted T-4 geometry, Table S1 and Fig. 1. Tetrahedral

configuration can be detected by measuring the angle subtended by two planes, each encompassing the silver and two adjacent ligands. Square-planar complexes exhibit tetrahedral angle equals 0° . For tetrahedral complexes, the tetrahedral angle equals 90° . In SCP1 the angle of the two planes; S2Ag1S2 and N4Ag1S2 is 86.97° supporting the tetrahedral topology of Ag atom. Two silver atoms and two sulfur atoms form rhombic mini-cycle (Ag_2S_2) motif via the long Ag1-S2 bond lengths while the short one connects two rings, as shown in Figs. 1b,c.

On the other hand, each rhombic mini-cycle (Ag_2S_2) motif connects another four Ag2 dimeric units (two 4- and two 8-membered rings) through Ag-S coordinate bonds to give rise to 3D-network structure, Figs 1d, 2 and 3. Interestingly, the distance between the two Ag atoms in the rhombic mini-cycle rings equals to $3.4636(17) \text{ \AA}$ in addition to other two argentophilic interactions in the network structure; mainly $3.2593(17)$ and $3.3429(16) \text{ \AA}$. These bond lengths are obviously shorter than the van der Waals contact distance for Ag-Ag ($4.26 \text{ \AA}$) [27] and longer than that in metal silver ($2.89 \text{ \AA}$). The mini-cycle [$\text{Ag}_2(\mu^3\text{-S}_2)$] motifs can be considered the main building blocks of SCP1 while the network structure exhibits three different argentophilic interactions. Thus, in view of the current discussion of argentophilic interactions [28], one might suggest that the formation of a [$\text{Ag}_2(\mu^3\text{-S}_2)$] rhomb is triggered by a weak, but non-negligible, Ag...Ag interaction. The repeated appearance of the unusual rhombic (Ag_2S_2) motif causes the formation of fused polygons mainly 8 atomic [$\text{Ag}_2\text{S}_2(\text{SCN})_2$], 12 atoms [$\text{Ag}_4\text{S}_2(\text{SCN})_2$], 18 atomic [$\text{Ag}_5\text{S}(\text{SCN})_4$] and 20 atomic [$\text{Ag}_6\text{S}_2(\text{SCN})_4$] rings, as shown in Figure S2, creating 3D-network. The case, which raises the question of whether the mini-cycle (Ag_2S_2) motifs with argentophilic interactions therein are the basic cause of the existence of SCP1. The structure of SCP1 extends three-dimensionally via coordinate bonds creating stair like structure, Fig. 2. The 3-D network contains nanometer voids with average size of ($34.84\text{-}58.46 \text{ nm}$), as can be seen in Fig 3. In addition to the strong

coordinate bonds, the 3D-structure of SCP1 is further packed by efficient short Van der Waals contacts (2,475-3.411 Å)

3.2 Characterization and morphology of SCP1 and nanosized 2

SCP1 and nanosized 2 phase purity are checked by measuring their powder X-ray diffractions (PXRD) which are quite similar to the simulated pattern produced by single crystal diffraction data of 1, Fig. 4. The data indicate that nanosized 2 is iso-structure to the crystal structure of SCP1. Broadening of the peaks of the PXRD pattern supports nanosized features of the particles. Moreover, the XRPD patterns of 2 were measured before and after the catalytic process displaying the same Miller indices (hkl) values which indicate high stability of 2 as a heterogeneous catalyst after photo-catalytic process, Fig. 4. Transmission Electron Microscopy (TEM) is used to measure morphology and the particle size of 2. TEM image with high magnification of 2 indicates regular spherical-like micro nano-structure exhibiting particle size in the range of 7.23–8.88 nm, Fig. 5.

3.3 Electronic absorption spectra, luminescence and sensing studies

The UV spectrum of SCP1 was measured in solid state exhibiting one absorption band at 319 nm due to π - π^* transition Fig. S3, with an optical band-gap of 3.88 eV while the photo luminescent (PL) spectrum in solid state displays an intense luminescent band at 368 nm at λ_{ex} = 340 nm corresponding to the close lying π - π^* transition Fig. S6. The variable quenching efficiencies of different solvents and metal ions on PL spectrum of SCP1 attract considerable attention because the good ability of SCP1 to act as photo-chemical device, Figs. 6, 7. The PL band of SCP1 in MeCN shows the highest intensity meanwhile the band intensity exhibits variable quenching ability in other solvents while the most quenching efficiency was observed for NB, Fig. 6. So, the quenching character of NB can be used for determination of NB selectively where the intensity of SCP1 band decreases gradually as the NB concentration was varied from 10 to 270 μ M. The quenching efficiency (QE) was

calculated according to the relation; $QE = (I_0 - I) / I_0 \times 100\%$. The QE was found to be 96.18% at NB concentration 270 μM indicating the highest quenching percentage of NB against SCP1 fluorescence, Fig.S5. The Stern-Volmer constant (K_{sv}) was calculated according to Eq (2) to be $5.55 \times 10^3 \text{ M}^{-1}$ which verifies the linear behavior of the Stern-Volmer curve at low [NB], Fig. 6c. The K_{sv} value seems similar to the reported sensors of NB [29, 30].

$$\frac{I_0}{I} = 1 + K_{sv}[M] \quad (2)$$

I_0 and I represent the PL intensities of SCP1 without NB and in presence of NB while quenching constant and NB concentration are represented by K_{sv} and $[M]$, respectively. The limit of detection (LOD) was calculated according to the equation [31]: $LOD = 3\sigma/k$ (σ is the standard deviation for the intensity of SCP1 in absence of NB, while k is the slope between the luminescence intensity and concentration, Fig. S6. LOD value ($1.723 \times 10^{-6} \text{ M}$) is lower compared to ($5.4 \mu\text{M}$) value which is accepted by the U.S. Environmental Protection Agency (EPA) [5, 32]. The properly LOD and the effectively high QE support the reality that SCP1 is an environment friendly sensor for selective determination of NB. The mechanism of quenching of NB is mentioned utilizing the photo-induced electron switch approach [33]. Electron poor character of NB facilitates electron switch from the conduction band; CB of SCP1, during the excitation, to the valence band; VB of NB leading to luminescence quenching. Otherwise, an efficacious energy is conveyed via the thiocyanate π -conjugated orbitals in SCP1 to NB, inducing PL quenching as was supported by the fluorescence resonance transfer (FRET) approach [34].

Also, the PL behavior of SCP1 can be utilized for selective determination of different metal ions. The PL intensity suffers lowering according to the kind of the metal ion meanwhile Fe^{3+} ion exhibits the higher quenching behavior, Fig. 7. So, the selective sensing ability of SCP1 for metal ions should be used for quantitative estimation of Fe^{3+} ion. The PL

intensity of SCP1 suffers gradual decrease upon increasing Fe^{3+} ion concentration in the range of 10-330 μM , Fig. 7b. The plot of Stern–Volmer is linear up to 45 μM suffering deviation from being linear at higher concentrations, Fig. 7c. QE, LOD and K_{sv} for Fe^{3+} ion are estimated giving the values of 97.57 %, 4.53 μM and $4.08 \times 10^{-3} \text{ M}^{-1}$, respectively, which are close to the reported values of the prototype compounds, Figs S7, S8 [5, 35]. SCP1 can be considered as an excellent PL sensor for quantitative determination of Fe^{3+} ion because low LOD and high QE. The mechanism of quenching phenomenon of Fe^{3+} ion is discussed according to the FRET approach where PL quenching resulted via the interfere of the electronic transition band of Fe^{3+} ion with the PL band of SCP1, as well as the effect of Lewis acidic Fe^{3+} cation on SCP1 resulting PL quenching [36].

3.4 Catalytic and photocatalytic degradation studies of nanosized 2

The photocatalytic activity of nanosized 2 was investigated in the presence of H_2O_2 as eco-friendly nature using Acid Blue 92 (AB-92) and Eosin-Y (EO-Y) dyes as target pollutants. (AB-92) and (EO-Y) dyes exhibit high stability leading to hard decomposition in waste streams. The mineralization processes were carried out by measuring the absorption spectra of (AB-92) and (EO-Y) at 560 and 514 nm, respectively. The visible spectra of control reactions in presence of AB-92 and EO-Y dyes and H_2O_2 at ambient conditions exhibit $D\% = 10.89\%$ and 10.02% within 160 min, respectively, Figs. S9, S10. In this case, there is no worth mineralization of the tested dyes without using a catalyst. Interestingly, the spectra of AB-92 and EO-Y dyes suffer obvious gradual decrease of the peaks intensity in the presence of the nanosized 2 and H_2O_2 while on subjecting UV-light or ultrasonic irradiation to the reactors, the peak intensities decrease dramatically during short times, Table 2. The rate of mineralization as well as the removal efficiency of the tested dyes exhibit notable increase according to the order ultrasonic irradiation > UV-light > room temperature [in case of AB-92 dye, $D\% = 97.89$ (within 35 min), 89.47 (within 105 min) and 89.47 (within 160

min), respectively, Fig. 8 and for EO-Y dye, D%= 99.36 (within 48 min), 89.24 (within 105 min) and 81.04 (within 145 min), Fig. 9, respectively], Table 2. The mineralization efficiency of nanosized **2** for AB-92 and EO-Y dyes reaches a highest value on using H₂O₂ and ultrasonic irradiation within very short time. The clear enhancements of photocatalytic degradation rates of the dyes support the energetic character of **2** for complete degradation of the tested dyes.

First order kinetic equations are applied to study the degradation reaction with respect to [dye]₀ concentration where the [H₂O₂]₀ initial concentration was excess 10-fold more than the [dye]₀. k_{obs} (observed rate constant) was calculated according to Eq. (3).

$$\ln \frac{A_o}{A_t} = K t \quad (3)$$

A₀ and A_t are the absorbance of dyes at time = 0 and t, respectively. The linear relationships support that the degradation reaction obeys pseudo first order rate relative to [dye]₀, Table 2 and Figs. S11, 12. The specific rate constant (k) was calculated using equation $k = k_{obs}/[H_2O_2]_0$, Table 2.

To address reusing of the catalyst, it was cleaned by deionized H₂O and dried at the end of the first use and then after a new experiment was carried out. The catalyst **2** exhibits the same catalytic activity for two cycles of the dye oxidation under ultrasonic irradiation, Fig. 10. After the second recycle, the time and efficiency of degradation remain steady as those at typical conditions while the degradation efficiency decreases slightly till the fourth cycle. The experimental PXRD patterns of nanosized **2** before and after mineralization reactions were recorded showing very good similarity compared to the simulated XRD pattern of SCP1 indicating that the sample of nanosized **2** has the same structure of the single crystals preserving its phase purity and stability as heterogeneous catalyst, Fig. 4. These results are further confirmed by elemental analysis.

3.5 Active species and mechanism of the catalytic and photo- catalytic processes

Identification of the type of the active species created in the EO-Y/ nanosized **2**/ H₂O₂ system, mainly •OH, h⁺, and O₂^{•-}, requires some investigations using isopropanol (IPA), ammonium oxalate (AO), or benzoquinone (BQ) as scavengers, respectively. IPA, AO or BQ added to EO-Y / nanosized **2**/ H₂O₂ system decreased the degradation efficiency of EO to 76.20% in 140 min, 66.20% within 140 min and 32.50% within 140 min, respectively, [Table 2, Figs. S13-16](#). In this case, the •OH active species have been quenched significantly by IPA while h⁺, and O₂^{•-} active species exhibit, relatively lower quenching effect by AO and BQ, respectively. The case which indicates that the catalytic process is highly affected by the formation rate of the •OH radicals than the h⁺, and O₂^{•-} active species.

For further support of the activity of •OH radicals terephthalic acid disodium salt (TANa) PL probing technology was applied which linked selectively with hydroxyl radicals to produce the fluorescent 2-hydroxy terephthalic acid (HTA) [\[37\]](#), The fluorescence intensity of catalyst**2** /H₂O₂ /TANa component elevated rapidly to 950 within 56 min supporting that •OH species are really produced in solution, [Fig. 12a](#). Consequently, when the tested dye and TANa are both put to the solution, the intensity of fluorescence spectra decreased apparently reaching only to 230 within 64 min, [Fig. 12b](#). It is obvious that some of the •OH radicals are subjected to fast oxidation to the dye, as rapid fading of the dye color was also noticed during recording the spectra. For that, consulting the data, a mechanism can be postulated which involves an interaction between H₂O₂ and the tested catalyst with generating highly active oxidizing species, mainly •OH radicals.

The hydroxyl radicals react with the tested dyes to propagate the reaction to intermediates leading to degradation products.

Other reactions are also possible as indicated by Eqs. (8 and 9).

The peroxide radicals ($\text{HO}_2^{\bullet-}$) can further oxidize other species present in the solution [38].

In addition to that the degradation efficiency of the dye is enhanced at normal conditions upon utilizing UV- light or ultrasonic radiation where irradiation improved producing of $\bullet\text{OH}$ radicals. H_2O_2 as a green oxidant in addition to the use of light irradiation can create $\bullet\text{OH}$ radicals as indicated in Eq (11):

The high occupied molecular orbital containing electrons of the nanosized **2** defined as the valence band (VB) can be excited under the UV-radiation to the lowest unoccupied orbital the conduction band (CB). The electron transfer causes production of a similar quantity of positive holes (h^+) which leave the VB, Eq. (12). The $\bullet\text{OH}$ radicals are formed via the addition of H^+ to $\text{O}_2^{\bullet-}$ produced by the reduction of O_2 by e^- , Eqs (13-16) and the oxidation of H_2O by h^+ creating $\bullet\text{OH}$, Eq (17). The $\bullet\text{OH}$ radicals oxidize the IC dye converting them to degradation products, CO_2 and H_2O , Eqs. (6, 7).

On the other hand, H₂O splits by ultrasonic irradiation [] as shown in Eqs (18-20).

The ultrasonic radiation assisted decomposition of H₂O₂ in the reaction medium according to Eqs (21-23).

At the end, the •OH radicals oxidize the tested dyes producing final oxidation products according to Eqs. (6 and 7).

4 Conclusion

The structures of SCP1 and nanosized 2 represent single crystals and micro nano-particles prepared by self-assembly and green method of ultrasonic radiation, respectively. 3D-framework is constructed via coordinate bonds and the unique mini-cycle (Ag₂S₂) motif. The fluorescence behavior and high quenching efficiency of SCP1 for Fe³⁺ ions and NB lead to be considered as a good and efficient candidate for selective detection of Fe³⁺ ion in presence of other metal ions and explosives. The UV-and ultrasonic radiation-catalytic processes presented in this study proved to be propitious devices for the elimination of non-biodegradable dyes like AB and EO dyes. The tested catalyst 2 acts as heterogeneous micro nano-catalyst for the efficient elimination of dyes in wastewater within relatively short times

mainly via $\bullet\text{OH}$ radicals according to (TANa) PL probing technology. The tested dyes follow the Fenton process which can be considered a powerful AOP, due to the fact that AOP does not need special equipment or energy input and capable to oxidize various organic pollutants utilizing the high oxidation potential of the $\bullet\text{OH}$ radical.

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Table 1 Crystal data and structures refinement parameters of the SCP1.

Chemical formula	C ₁ Ag ₁ N ₁ S ₁
Formula weight	165.95
Crystal system	Monoclinic
Space group	C1 2/c 1
<i>a</i> (Å)	8.815(5)
<i>b</i> (Å)	7.988(5)
<i>c</i> (Å)	8.207(4)
α (°)	90
β (°)	93.766(16)
γ (°)	90
<i>V</i> (Å ³)	576.7(5)
<i>Z</i>	8
<i>D</i> _{calcd} (g/cm ³)	3.82
Absorption coefficient, mm ⁻¹	7.385
<i>F</i> (000)	608
Crystal size, mm	0.040 x 0.070 x 0.090
θ range, deg	1.213– 34.630
Index range <i>h</i> , <i>k</i> , <i>l</i>	-23 / 23, 0/ 17, 0/ 46
<i>R</i> _{int}	0.037
Data/restraint/parameters	3980/0/ 38
Goodness of fit on <i>F</i> ²	1.0882
Final <i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0432, 0.1400
$\Delta\rho_{\text{max}}$, eÅ ⁻³ , $\Delta\rho_{\text{min}}$, eÅ ⁻³	1.21, -1.75
CCDC NO	2007622

Table 2 The kinetic parameters for the photodegradation of AB-92 and EO-Y dyes using nanosized **2**

Catalyst	Condition	Irradiation Time (min)	Removal %	K (min ⁻¹)	R ²
Non	AB-92 + H ₂ O ₂	160	11.89	6.44×10^{-4}	0.984
Nanosized 2	AB-92/ Room + H ₂ O ₂	160	83.33	0.0097	0.994
Nanosized 2	AB-92 / UV + H ₂ O ₂	105	83.43	0.0176	0.997
Nanosized 2	AB-92 /Sonication + H ₂ O ₂	35	92.71	0.0595	0.968
Non	EO-Y + H ₂ O ₂	160	10.02	4.74×10^{-4}	0.981
Nanosized 2	EO-Y / Room + H ₂ O ₂	145	73.25	0.00932	0.998
Nanosized 2	EO-Y / UV + H ₂ O ₂	105	84.2	0.0171	0.996
Nanosized 2	EO-Y / Sonication +H ₂ O ₂	38	93.76	0.0573	0.954
Nanosized 1	EO-Y / UV +H ₂ O ₂ +AO	140	68.46	0.0095	0.971
Nanosized 1	EO-Y / UV +H ₂ O ₂ +BQ	140	56.96	0.0063	0.992
Nanosized 1	EO-Y / UV +H ₂ O ₂ +IPA	140	29.33	0.0027	0.988

Figure 1 (a) Asymmetric unit of AgSCN showing atom labeling scheme, (b) view of tetrahedral geometry of AgSCN along a-axis, (c) packing structure showing the complex connections via quadrominicyclic (Ag_2S_2) motifs extending the structure three dimensionally, (d) view of the distorted polygonal rings

Figure 2 View of the 3D-network structure of SCP1 showing the stair construction along the b-axis

Figure 3 Visualization of the 3D-network structure of SCP1 down the projection of the a - axis showing the pore structure

Figure 4 PXRD patterns: (a) simulated pattern based on single crystal data of SCP1; (b) SCP1 as synthesized by self-assembly method; (c) nanosized **2** before degradation process; (d) nanosized **2** after degradation process

Figure 5 The TEM image of **2** showing the nanosized particles

Fig. 6. (a) Luminescence spectra of SCP **1** in different organic solvents, (b) Effect on the emission spectra of SCP **1** suspended in MeCN with the addition of NB concentrations and (c) Stern–Volmer plot of I_0/I versus the NB ion concentration. Inset: the fluorescence quenching linearity relationship at low NB concentrations.

Fig. 7.(a) Luminescence spectra of SCP **1** in aqueous solutions upon gradual addition of different metal ions (10^{-3}M); (b) Effect on the emission spectra of SCP **1** suspended in MeCN with the addition of Fe^{3+} concentrations and (c) Stern–Volmer plot of I_0/I versus the Fe^{3+} ion concentration. Inset: the fluorescence quenching linearity relationship at low Fe^{3+} concentrations.

Fig. 8. Temporal evolution of the spectra during the photodegradation of AB-92 dye in the presence of nanosized **2** under (a) Room temperature; (b) under UV-light irradiation; (c) under ultrasonic irradiation and (d) Results of photocatalytic decomposition of AB-92 dye under different irradiation source.

Fig. 9. Temporal evolution of the spectra during the photodegradation of EO-Y dye in the presence of nanosized 2 under (a) Room temperature; (b) under UV-light irradiation; (c) under ultrasonic irradiation and (d) Results of photocatalytic decomposition of EO-Y dye under different irradiation source.

Fig. 10. The recycle runs of the photodegradation of EO-Y dye (2.5×10^{-4} M) and H_2O_2 (0.1 M) in presence of nanosized **2** under UV-light irradiation.

Fig. 11. Effect of different scavengers on the Photo-degradation of EO-Y dye in the presence of nanosized **1** under UV-light irradiation

Figure 12 Fluorescence spectra of the solution containing the nanosized **2** catalyst/H₂O₂ system and NaTA ($\lambda_{\text{ex}} = 340$ nm) (a) in absence of AB-92 dye and (b) in presence of AB-92 dye

Figures

Figure 1

(a) Asymmetric unit of AgSCN showing atom labeling scheme, (b) view of tetrahedral geometry of AgSCN along a-axis, (c) packing structure showing the complex connections via quadro minicycle (Ag₂S₂) motifs extending the structure three dimensionally, (d) view of the distorted polygonal rings

Figure 2

View of the 3D-network structure of SCP1 showing the stair construction along the b-axis

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PXRD patterns: (a) simulated pattern based on single crystal data of SCP1; (b) SCP1 as synthesized by self-assembly method; (c) nanosized 2 before degradation process; (d) nanosized 2 after degradation process

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The TEM image of 2 showing the nanosized particles

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(a) Luminescence spectra of SCP 1 in different organic solvents, (b) Effect on the emission spectra of SCP 1 suspended in MeCN with the addition of NB concentrations and (c) Stern–Volmer plot of I_0/I versus the NB ion concentration. Inset: the fluorescence quenching linearity relationship at low NB concentrations.

Figure 7

(a) Luminescence spectra of SCP 1 in aqueous solutions upon gradual addition of different metal ions (10–3M); (b) Effect on the emission spectra of SCP 1 suspended in MeCN with the addition of Fe^{3+} concentrations and (c) Stern–Volmer plot of I_0/I versus the Fe^{3+} ion concentration. Inset: the fluorescence quenching linearity relationship at low Fe^{3+} concentrations.

Figure 8

Temporal evolution of the spectra during the photodegradation of AB-92 dye in the presence of nanosized 2 under (a) Room temperature; (b) under UV-light irradiation; (c) under ultrasonic irradiation and (d) Results of photocatalytic decomposition of AB-92 dye under different irradiation source.

Figure 9

Temporal evolution of the spectra during the photodegradation of EO-Y dye in the presence of nanosized 2 under (a) Room temperature; (b) under UV-light irradiation; (c) under ultrasonic irradiation and (d) Results of photocatalytic decomposition of EO-Y dye under different irradiation source.

Figure 10

The recycle runs of the photodegradation of EO-Y dye (2.5×10^{-4} M) and H₂O₂ (0.1 M) in presence of nanosized 2 under UV-light irradiation.

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Figure 12

Fluorescence spectra of the solution containing the nanosized 2 catalyst/H₂O₂ system and NaTA ($\lambda_{\text{ex}} = 340$ nm) (a) in absence of AB-92 dye and (b) in presence of AB-92 dye

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