Photodegradation of rhodamine-B and methyl orange employing nano-alumina developed from new aluminium(III) complex(es) associated with phenanthridine-salicylaldehyde derived ligands

Sathish Thanigachalam, Madhvesh Pathak and Kulathu Iyer Sathiyanarayanan

Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore, Tamil Nadu, India

ABSTRACT
A series of five new heteroleptic mononuclear derivatives of aluminium(III) have been synthesized and characterized. Complexes \( [(\text{CH}_3\text{COCH}_2\text{COCH}_3)_2\text{Al}(1\text{a})] 2\text{a} \), \( [(\text{CH}_3\text{COCH}_2\text{COCH}_3)_2\text{Al}(1\text{b})] 2\text{b} \), \( [(\text{CH}_3\text{COCH}_2\text{COCH}_3)_2\text{Al}(1\text{c})] 2\text{c} \), \( [(\text{CH}_3\text{COCH}_2\text{COCH}_3)_2\text{Al}(1\text{d})] 2\text{d} \) and \( [(\text{CH}_3\text{COCH}_2\text{COCH}_3)_2\text{Al}(1\text{e})] 2\text{e} \) were obtained by treating \( \text{Al(OPr}^\text{i}_3\text{)} \) with acetylacetone and bidentate ligands (developed by treating phenanthridine and salicylaldehyde) \( 1\text{a}–1\text{e} \) in 1:2:1 stoichiometry using anhydrous benzene as solvent. All the newly synthesized aluminium(III) complexes were characterized by NMR (\(^1\text{H and }^{13}\text{C})\), FTIR, HPLC, HRMS and elemental analysis. Derivatives \( 2\text{a}-2\text{e} \) were confirmed by dept-135 and HSQC also. Complex \( 2\text{a} \) was employed as precursor for the synthesis of active alumina by well-established sol-gel technique. Nanostructured alumina was confirmed by powder XRD, FTIR, TGA-DTA and BET surface area, Fe-SEM and TEM analyses. Alumina synthesized from \( 2\text{a} \) was used for photodegradation of rhodamine-B and methyl orange dyes that resulted in remarkably high (>93%) decolorization within 140 minutes exposure of natural sunlight.
1. Introduction

Aluminium is among the most abundant elements existing on the earth’s crust and has a wide range of applications in various industries [1]. Complexes of aluminium(III) with Schiff bases have gained popularity due to their significant catalytic activity towards polymerization of ethylene [2], methacrylate [3], ring-opening polymerization of lactides [4], caprolactone [5], insertion of CO₂ into oxiranes [6] and organic light emitting devices as heterocyclic complexes. In addition, reaction of Al(OPr_)₃ with various other potential ligands like β-diketones [7], diols [8], β-ketoesters [9], oximes [10], bisphenolates [11], bipherolatephosphines [12], oxazoline-amido-phenolate [13] and amine bisphenols [14] tend to alter the steric and electronic environment around aluminium [15].

A series of new metallo-organic derivatives of aluminum(III) were synthesized from aluminium(III) isopropoxide modified by tridentate and β-diketones/8-hydroxyquinoline which were efficient precursors for obtaining nano-alumina by sol-gel [16]. Pure α-Al₂O₃ nano-rods were reported by Sanwaria et al. by sol-gel technique from four- and six-coordinate complexes produced by treating Al(OPr_)₃ with different salicylaldehydes [17] and 8-hydroxy quinolines [18] where six-coordinate aluminium(III) derivatives were preferred precursor. Cubic phase of γ-alumina was prepared from six-coordinate aluminium(III) complex incorporated with oxime ligand through sol-gel only [19]. A chemical modification in the precursor alters the electronic environment, which disturbs the kinetics of the hydrolysis process and eventually leads to change in surface morphology of the metal oxide nanoparticles [20]. These chemical alterations enhance the gelation time, sustained viscosity of the sol and form uniform mesoporous metal oxides in appreciable yield [21].

In order to explore a variety of applications, it has become a major requirement to modify the structures of the complexes via specific synthetic routes [22–24].

Alumina is amphoteric (acid-base characteristics), reflecting high surface area, mechanical, crystallinity and thermal durability too. Hence, alumina nanoparticles could be extensively employed in adsorption, catalysis as well as in several other fields including waste water treatment and electrical insulators [25]. A number of nanomaterials
have been reported with detailed study interpreting remarkable properties, structures and applications [26]. In view of interesting applications of nano-alumina, some reports on dye degradation have been well documented. Singh et al. demonstrated dye degradation through a greener route while utilizing various phases of nano-alumina obtained by recycling solid waste [27]. Further, photocatalytic capabilities of alpha and gamma forms of nano Al₂O₃ (obtained by “sol-gel” technique taking aluminium nitrate as precursor) have also been compared for direct black 122 and RY 145 and were found considerably higher (>95%) for alpha phase as compared to γ-alumina [28]. Another report appeared in 2016 on efficient photocatalysts to degrade orange G by γ-Al₂O₃ where nano aluminium oxide was prepared from aluminium chloride again by sol-gel route only [29]. Further, photodegradation of methylene blue was carried out on nano sized aluminium oxide (produced by “sol-gel” using conventional precursor aluminium chloride) where only 36% decolorization was observed in 3 h [30]. Very recently, another report described that zinc oxide doped γ-alumina required almost 4 h in degradation of amido black dye under ambient sunshine [31]. Thus, photocatalytic degradation of various toxic organic pollutants, e.g. brilliant green (BG), bisphenol A(BPA) [32], chromium(III) [33] and atomic layer deposition [34] have been established.

Phenanthridine supported salicylaldehyde derivatives were synthesized and optimized in our lab. The N and O atoms of these ligands possess sensing ability to detect Al³⁺, Th⁴⁺, picric acid [35], chemo sensor for detection of chromium(III) on real sample analysis [36], detection of aniline [37], cyanide [38] and organic/inorganic arsenic compounds are adsorbed by coral limestone of aluminium [39]. Thus, in continuation to significant aluminium complexes, nano-alumina, the present work deals with an effort to synthesize and characterize a series of new six-coordinate mononuclear aluminium(III) derivatives incorporated with phenanthridine based salicylaldehyde bidentate ligands [35, 36]. One of the newly synthesized representative complexes of aluminium was subjected to sol-gel technique to obtain nano-alumina that was employed for photodegradation of rhodamine-B and methyl orange. Higher performance in less time as compared to the results reported are observed.

2. Experimental

2.1. General

Metallo-organic derivatives of aluminium(III) are synthesized under stringent anhydrous conditions. Al(OPrⁱ)₃, acetylacetone, salicylaldehyde derivatives, ammonium acetate, ethanol, hexane, dichloromethane and NMR solvents were purchased from Sigma Aldrich and β-tetralone obtained from Aalfa Aesar. Benzene was outsourced from Spectrochem. Solvents such as benzene, hexane and dichloromethane were made anhydrous by reported methods [40]. The newly developed complexes were analyzed by ¹H, ¹³C and dept-135 spectra by recording data on a BRUKER ADVANCE III (400 MHz frequencies for ¹H NMR and 100 MHz frequencies for ¹³C NMR) spectrophotometer in CDCl₃, using TMS as internal reference standard. Chemical shift values are given in parts per million (ppm). The deuterated solvent (CDCl₃) peaks appear at 7.26 ppm and its moisture peak surfaced at 1.56 ppm. Melting point of all the synthesized complexes were
measured by Elchem digital melting point apparatus. FTIR spectra were recorded on a SHIMADZU IR affinity 1 (4,000–400) spectrometer with anhydrous KBr pellets. Elemental analysis of complexes was carried out on an Elementar VarioEL III instrument. UV-visible spectra were measured with a JASCO V-670 UV-VIS spectrophotometer. HPLC spectra of 2a–2e were recorded from a Waters 1525 Binary HPLC Pump. HRMS spectra of the aluminium(IV) complexes 2a–2e were collected from Waters-Xevo G2-XS-Q TOF. Powder XRD data collected from an X-ray BRUKER D8 Advance X-ray diffractometer. Thermal analysis was recorded on a SDT Q 600 Ta instrument. Surface area and pore diameter of obtained alumina were carried out with a Quantachrome USA instrument. Fe-SEM and EDX images were recorded on a FEI-Quanta 250 FEG (FE-SEM). TEM images of nano-alumina particles were obtained from a FEI-Technai G2 20 Twin instrument. Raman spectrum of alumina were recorded with a HORIBA scientific.

2.2. Synthesis of phenanthridine based salicylaldehyde derivative ligands

The ligands of this series have been prepared, purified and characterized as per the methods reported [35, 36]. The ligand derivatives 1a–1e were obtained from corresponding salicylaldehyde mixed with ammonium acetate in ethanol while warming the mixture for 10 minutes. Once the reaction mixture attained room temperature, 2-tetralone was added and the flask was sealed with a black cover and left for a couple of weeks. In order to monitor the progress, TLC was examined till completion of the reaction. Crude product was purified by column chromatography using silica gel (60e–120 mesh) to isolate pure solid products of ligands 1a–1e by using eluent solution (ethyl acetate and n-hexane). The structures of ligands were confirmed by FTIR and NMR (1H and 13C) spectra.

2.3. Synthesis of new aluminium(III) complexes

2.3.1. Synthesis of [(C5H7O2)2Al(1a)] (2a)

Benzene solution (ca. 15 mL) of aluminium isopropoxide (2.04 g, 10 mmol) was reacted with acetylacetone (2.03 g, 20 mmol) and 1a (3.751 g, 10 mmol) in 20 ml anhydrous benzene as solvent. The reaction mixture was refluxed on a fractionating column for 6 h. During reflux, the liberated isopropanol came out of the reaction mixture in the form of an azeotropic mixture that facilitated an estimate of the amount of liberated PrOH oxidimetrically [16, 40] to monitor the progress of reaction. After completion of the reaction, excess solvent was removed under vacuum and afterwards washed with anhydrous n-hexane repeatedly to afford a greenish-yellow solid. Yield: 5.10 g (85.2%). m.p = 252–254 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 1.99 (s, 12H, CH3 of acetylacetone), 2.79–2.82 (t, 2H, J = 6.4 Hz, CH2), 2.93–2.97 (t, 2H, J = 5.6 Hz, CH2), 3.04–3.07 (m, 2H, J = 4 Hz, CH2), 3.13–3.16 (t, 2H, J = 6.4 Hz, CH2), 5.482 (s, 2H, CH of acetylacetone), 6.54–6.58 (t, 1H, J = 7.6 Hz, ArH), 6.97–7.01 (t, 1H, J = 7.6 Hz, ArH), 7.06–7.09 (t, 2H, J = 8 Hz, ArH), 7.16–7.23 (m, 3H, J = 8 Hz, ArH), 7.28–7.35 (m, 4H, J = 6.8 Hz, ArH), 7.54–7.56 (d, 1H, J = 7.2 Hz, ArH). 13C NMR (100 MHz, CDCl3, 25 °C): δ (ppm) 26.78 (CH3 carbon of acetylacetone), 29.33, 29.39, 29.49, 32.88, 101.13 (CH carbon of acetylacetone) 118.15, 118.55, 122.49, 126.03, 126.24, 126.96, 127.31, 127.58, 127.97,
128.05, 128.35, 128.48, 129.44, 129.74, 130.31, 131.90, 132.56, 133.23, 138.28, 139.41, 147.75, 151.28, 156.35 (ArC-O), 157.21 (ArC=N), 191.48 (keto carbon of acetylacetone). FTIR (solid KBr) ν = 2956.87, 1583.56, 1526.69, 1382.96, 1286.52, 1247.94, 1190.08, 1026.13, 1014.56, 935.48, 736.81, 752.24, 682.80, 657.73, 576.72, 487.99, 418.55. Anal. Calcd for C37H34AlNO5: C, 74.11; H, 5.72; N, 2.34. Found: C, 74.02; H, 5.54; N, 2.43%. HRMS and HPLC spectra for 2a Calcd [M+]+ m/z 599.2252, Found: 599.2262.

Synthetic procedures of 2b–2e are similar to that of 2a; relevant data have been provided in Table 1.

### 2.3.2. Synthesis of [(C₅H₇O₂)₂Al(1b)] (2b)

Yield: 5.82 g (92.6%). m.p. = 264–266°C. The ¹H NMR spectrum of 2b exhibited a singlet at 3.86 ppm due to the presence of methyl protons and one new peak was observed at 56.09 ppm by ¹³C NMR from the presence of methyl carbon of methoxy moiety corresponding to the total number of H and C atoms as per the proposed structure of the aluminium derivative. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.919 (s, 12H, CH₃ of acetylacetone), 2.69–2.73 (t, 2H, J = 6.4 Hz, CH₂), 2.85–2.88 (m, 2H, J = 5.6 Hz, CH₂), 2.95–2.99 (m, 2H, J = 4 Hz, CH₂), 3.05–3.08 (t, 2H, J = 6.4 Hz, CH₂), 3.86 (s, 3H, CH₃), 5.40 (s, 2H, CH of acetylacetone), 6.47–6.51 (t, 1H, J = 8 Hz, ArH), 6.64–6.66 (d, 1H, J = 8 Hz, ArH), 6.73–6.75 (d, 1H, J = 8 Hz, ArH), 6.88–6.92 (t, 1H, J = 7.2 Hz, ArH), 7.07–7.14 (m, 2H, J = 7.6 Hz, ArH), 7.17–7.27 (m, 4H, J = 4 Hz, ArH), 7.45–7.47 (t, 1H, J = 8.4 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ (ppm) 26.78 (CH₃ carbon of acetylacetone), 29.33, 29.39, 29.41, 32.82, 56.09 (carbon of OMe), 101.13 (CH carbon of acetylacetone), 111.74, 118.13, 123.69, 123.76, 125.93, 126.20, 126.84, 127.43, 127.50, 127.93, 128.03, 128.34, 128.51, 129.50, 129.65, 132.62, 133.27, 138.25, 139.46, 146.63, 147.32, 149.19, 151.13 (ArC-O), 156.51 (ArC=N), 191.47 (keto carbon of acetylacetone). FTIR (solid KBr) ν = 2970.38, 1624.06, 1539.06, 1523.76, 1402.25, 1352.10, 1269.16, 1219.01, 1109.07, 1010.70, 950.91, 842.89, 790.81, 744.52, 690.52, 619.15.
2.3.3. Synthesis of [(C₅H₇O₂)₂Al(1c)] (2c)

Yield: 6.10 g (94.9%). m.p = 274–276 °C. Triplet at 1.49–1.52 ppm and multiplet at 4.12–4.17 ppm were observed due to presence of methyl and methylene protons of ethoxy group of 2c, respectively. A couple of new peaks at 15.01 ppm and 64.43 ppm were identified as methyl and methylene carbon atoms of -OEt moiety of 2c. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.49–1.52 (t, 3H, J = 6.8 Hz, CH₃), 1.99 (s, 12H, CH₃ of acetylacetonate), 2.77–2.81 (t, 2H, J = 6 Hz, CH₂), 2.93–2.96 (t, 2H, J = 6 Hz, CH₂), 3.02–3.05 (t, 2H, CH of acetylacetonate), 3.15 (s, 2H, CH₂), 4.12–4.17 (m, 2H, CH₂), 5.48 (s, 2H, CH of acetylacetonate), 6.55–6.59 (t, 1H, J = 8 Hz, ArH), 6.71–6.75 (d, 1H, J = 8 Hz, ArH), 6.82–6.83 (d, 1H, J = 8 Hz, ArH), 7.15–7.21 (m, 2H, J = 7.6 Hz, ArH), 7.28–7.31 (t, 2H, J = 6.4 Hz, ArH), 7.30–7.34 (d, 2H, J = 8 Hz, ArH), 7.34–7.36 (d, 2H, J = 6 Hz, ArH), 7.53–7.55 (d, 1H, J = 6.8 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 15.01 (CH₃), 27.78 (CH₃ carbon of acetylacetonate), 29.32, 29.40, 32.77, 64.43 (CH₂ of ethoxy group), 101.13 (CH carbon of acetylacetonate), 112.91, 118.23, 123.68, 124.03, 125.92, 126.18, 127.42, 127.89, 128.00, 128.34, 128.52, 129.35, 129.65, 132.66, 133.31, 138.25, 146.53, 147.15, 148.28 (ArC-O), 156.56 (ArC=N), 191.48 (keto carbon of acetylacetonate). FTIR (solid KBr) ν = 2942.44, 1581.63, 1527.62, 1382.96, 1286.52, 1247.94, 1159.22, 1026.13, 935.48, 817.82, 752.24, 684.73, 623.01, 576.72, 487.99. Anal. Calcd for C₃₉H₃₆AlNO₆: C, 72.77; H, 5.95; N, 2.18%. Found: C, 72.56; H, 5.70; N, 2.26%. HRMS for 2c calculated [M⁺] m/z 643.2515, Found: 644.2034.

2.3.4. Synthesis of [(C₅H₇O₂)₂Al(1d)] (2d)

Yield: 6.62 g (83.7%). m.p = 296–298 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.99 (s, 12H, CH₃ of acetylacetonate), 2.79–2.82 (t, 2H, J = 6.4 Hz, CH₂), 2.94–2.97 (t, 2H, J = 5.6 Hz, CH₂), 3.03–3.06 (m, 2H, J = 4 Hz, CH₂), 3.13–3.16 (t, 2H, J = 6 Hz, CH₂), 5.48 (s, 2H, CH of acetylacetonate), 6.94–6.96 (d, 1H, J = 8.8 Hz, ArH), 7.05–7.08 (t, 1H, J = 7.6 Hz, ArH), 7.20–7.27 (m, 3H, J = 7.6 Hz, ArH), 7.31–7.32 (t, 3H, J = 4 Hz, ArH), 7.35 (s, 2H, ArH), 7.54–7.56 (d, 1H, J = 6.8 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ (ppm) 26.78 (CH₃ of acetylacetonate), 29.25, 29.33, 29.43, 32.81, 101.13 (CH of acetylacetonate), 110.21, 120.00, 123.92, 126.12, 126.31, 127.26, 127.84, 128.05, 128.09, 128.18, 128.35, 128.53, 129.51, 129.69, 132.34, 132.41, 132.86, 134.07, 138.34, 139.39, 147.99, 149.57, 156.40 (ArC-O), 156.48 (ArC=N), 191.47 (keto carbon of acetylacetonate). FTIR (solid KBr) ν = 2951.09, 1591.27, 1527.62, 1382.96, 1286.52, 1247.94, 1192.01, 1159.22, 1026.13, 935.48, 817.82, 752.24, 684.73, 623.01, 576.72, 487.99. Anal. Calcd for C₃₇H₃₃AlBrNO₅: C, 65.49; H, 4.90; N, 2.06%. Found: C, 65.69; H, 4.95; N, 2.05%. HRMS for 2d calculated [M⁺] m/z 677.1357, Found: 677.1361.

2.3.5. Synthesis of [(C₅H₇O₂)₂Al(1e)] (2e)

Yield: 5.6 g (87.8%). m.p = >300 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.922 (s, 12H, CH₃ of acetylacetonate), 2.76–2.79 (t, 2H, J = 6.4 Hz, CH₂), 2.89–2.92 (m, 2H, J = 5.6 Hz, CH₂), 2.98–3.01 (m, 2H, J = 3.6 Hz, CH₂), 3.08–3.11 (t, 2H, J = 6.8 Hz, CH₂), 5.40 (s, 2H,
CH of acetylacetonate), 6.91–6.95 (t, 1H, J = 7.6 Hz, ArH), 7.02–7.04 (d, 1H, ArH),
7.10–7.12 (d, 1H, ArH), 7.15–7.19 (m, 1H, J = 7.2 Hz, ArH), 7.24–7.31 (m, 4H, J = 4.4 Hz,
ArH), 7.49–7.51 (t, 1H, J = 5.6 Hz, ArH), 7.98–8.01 (m, 1H, J = 2.4 Hz, ArH), 8.03–8.04 (d,
1H, J = 2.8 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ (ppm) 26.78 (CH₃ carbon of
acetylacetonate), 29.16, 29.29, 29.49, 32.64, 101.13 (CH of acetylacetonate), 118.80,
121.02, 125.74, 126.43, 127.74, 127.90, 128.18, 128.34, 128.47, 128.55, 128.93, 130.19,
131.90, 132.05, 138.56, 139.24, 139.31, 148.53, 148.61, 156.01 (ArC-O), 164.03 (ArC-N),
191.47 (keto carbon of acetylacetonate). FTIR (solid KBr) ν = 2922.16, 1583.56, 1521.84,
1460.11, 1381.03, 1357.89, 1286.52, 1190.08, 1010.70, 933.55, 771.53, 684.73, 657.73,
574.79, 484.13. Anal. Calcd for C₃₇H₃₃AlN₂O₇: C, 68.94; H, 5.16; N, 4.35%. Found: C,
68.82; H, 5.08; N, 4.45%. HRMS for 2e calculated [M⁺] m/z 644.2103, Found: 645.1630.

2.4. Synthesis of nano sized Al₂O₃ from 2a by sol-gel technique

Three grams of 2a was dissolved in anhydrous EtOH while stirring the solution followed
by adding 5 ml concentrated HCl. Afterwards, a solution (ca. 2 mL) of water and
ethanol in (1:5) was added to the yellow suspension in an interval of 4–6 h and excess
amount of water was added continuously followed by stirring for 2 days. The obtained
gel was preheated in a hot air oven at 110 °C for 24 h to get xerogel, that was ground
later to get white creamy powder. Powder was washed with distilled water and acet-
one several times to remove impurities. The final product was divided into 3 portions,
and these portions were sintered in a muffle furnace at 800 °C, 1000 °C and 1200 °C
for 4 h to get Al₂O₃.

2.5. Photodegradation of dyes by alumina

The organic pollutants rhodamine-B and methyl orange (Figure 1) are degraded by
using newly synthesized nano-alumina because it acted as an efficient dye adsorbent
material. Photodegradation experiments of dyes were carried out in natural sunlight.
The results of this procedure depend upon parameters like initial concentration of
dyes and alumina, contact time, temperature, pH range, etc. Three different amounts,
0.030, 0.040 and 0.050 grams, of adsorbent were dispersed in 50 ml of both dye solu-
tions (100 mg/L) and H₂O₂ added as initiator with continuous stirring followed by dou-
ble distilled water as a dispersion medium. The whole reaction was kept in dark
conditions for 30 mins and then in direct sunlight. Three ml of sample was taken
every 20 minutes and centrifuged. The absorption of supernatant solution was deter-
mined by UV-VIS. Absorptions of these samples were measured from 200 to 800 nm,

Removal (Adsorption) efficiency (%) = \frac{Co–Cf}{Co} × 100 \tag{1}

where C₀ and C_f are initial and final concentrations (mg/L) of dye solutions.
3. Results and discussion

3.1. Synthesis and structural determination

All the ligands (1a–1e) utilized herein were prepared and analyzed in our lab as per the reported synthetic procedure (Scheme 1) [35, 36]. Afterwards, under stringent anhydrous conditions new Al(III) complexes were prepared by one pot reaction of Al(OPr)i3 and acetylacetone with corresponding ligands (1a–1e) in 1:2:1 stoichiometric molar ratio in dried benzene giving 2a–2e as displayed in Scheme 2. The progression in the reaction was monitored continuously with oxidimetrically [40, 41] determining liberated isopropanol in the azeotrope (PrOH + C6H6) collected in cold conditions. After observing no production of isopropanol from 6 to 8 h, extra solvents were removed by vacuum pump to furnish yellowish solid products in more than 83% yield. The crude products were purified with 2–3 washings of n-hexane and further attempted to obtain quality crystals in a mixture of n-hexane and dichloromethane.

These aluminium complexes are fairly soluble in most organic solvents, e.g. chloroform, isopropanol, methanol, dichloromethane, toluene, benzene as well as in acetonitrile. Structural characterization of 2a–2e was established by elemental analysis, UV-VIS, NMR (1H, 13C) and FTIR spectroscopic techniques as exhibited in Supporting Information (SI) Figures S1–S25 and S36–S40, respectively. In addition, the purity and existence (mol. wt.) of 2a–2e could be verified with HPLC and HRMS spectra displayed in SI Figures S26–S30 and S31–S35, respectively. Simultaneously, dept-135 and HSQC spectra of 2a are also available as Figures S4 and S5 in SI.
3.2. NMR studies

$^1$H NMR spectra of 2a–2e exhibited disappearance of free OH peaks from ligands (acacH and 1a–1e) that is the indication for attachment with Al. Further, presence of two new singlet peaks at 1.91–1.99 ppm and 5.40–5.48 ppm are signatures of four methyl groups and a pair of methyne protons, respectively, is another evidence for acetylacetonate moiety to be coordinated with aluminium in the final complexes. $^{13}$C NMR also revealed resonances at 26.78 ppm, 101.13 ppm and 191.47–191.48 ppm (downfield as compared to free acetylacetone) due to methyl, methyne and carbonyl carbons of acetylacetonate, respectively.

At the same time, two sets of CH$_2$ aliphatic protons were observed at 2.69–2.99 ppm and remaining aromatic protons appeared at 6.47–8.04 ppm as expected. $^{13}$C NMR spectra of the aluminium derivatives exhibit four aliphatic carbons at 29.16–32.88 ppm and aromatic carbons 110.21–164.03 ppm. Thus, characteristic patterns for 2a–2e indicate six-coordination of the ligands around aluminium in monomeric (Scheme 2) final products as yellowish solids in appreciable yields (> 80%).

3.2.1. Depth-135 NMR and HSQC

Further, 2a was confirmed with dept-135 NMR spectrum and HSQC. The total count of 37carbon atoms existed and among those four CH$_3$ groups of acetylacetonate appear
in positive mode in one single peak at 26.78 ppm and CH also appears in positive mode at 101.13 ppm. Aliphatic CH\textsubscript{2} of ligand moiety stands in negative mode at 29.33–32.88 ppm while all these four CH\textsubscript{2} groups appear as individual signals. Remaining aromatic CH appear in positive mode at 118.5–131.90 ppm; the spectrum is revealed in SIFigure S4.

Similarly, 2b exhibits two new peaks at 26.78 and 56.09 ppm from methyl (of acetylacetonato) and methoxy methyl (of 1b) in positive mode and CH\textsubscript{2} groups of ligands in negative mode as discrete peaks; the spectrum is shown in SI Figure S9. Complex 2c displayed two sharp peaks at 15.02 (CH\textsubscript{3} for ethoxy moiety) and 26.80 ppm (CH\textsubscript{3} of acetylacetonato) in positive mode and one new single peak in negative mode at 64.50 ppm (CH\textsubscript{2}) corresponding to acetylacetonato; remaining CH\textsubscript{2} groups of 1c are in the range of 29.32 to 32.38 ppm as displayed in SI Figure S14. Further, acetylacetonato moieties of 2d appear as sharp peak in positive mode at 26.78 (CH\textsubscript{3}), 101.14 ppm (CH) while remaining CH\textsubscript{2} groups of 1d are in negative mode as single discrete peaks from 26.09 to 29.50 ppm in the spectrum displayed as SI Figure S19. Methyl and methyne groups of 2e appeared at 26.78 and 101.14 ppm in positive region. Aliphatic CH\textsubscript{2} of 1e is at 29.15 to 32.64 ppm as individual peaks evident in SI Figure S24.

In addition, Heteronuclear Single Quantum Coherence (HSQC) spectra of 2a, 2b, 2c, 2d and 2e were found as per the expectations to satisfy the structural pattern of the complexes (SI Figures S5, S10, S15, S20 and S25).

### 3.3. FTIR spectra

Authentic bonding pattern in all these newly synthesized Al(III) complexes could be verified easily while comparing the characteristic stretching frequencies of aluminium derivatives with relevant free ligands. Disappearance of broad OH peaks (> 3000 cm\textsuperscript{−1}) from corresponding free ligands and appearance of new strong peaks at 683–691 cm\textsuperscript{−1} confirmed Al-O bond formation after deprotonation of ligands. The sharp peaks at 559–575 cm\textsuperscript{−1} in IR spectra of all the complexes are evidence for Al-N bonding. Vibrational spectroscopy reveals the C=O stretch shifted from 1735 to 1582–1624 cm\textsuperscript{−1} due to its decreased bond order to exhibit bidentate quasiaromatic acetylacetonate with a strong band at 1522–1528 cm\textsuperscript{−1} \cite{42} because of C=C bond. The phenolic stretch of C-O could be easily spotted as a strong peak at 1287–1288 cm\textsuperscript{−1} in all the ligands involved herein \cite{43}. The FTIR spectra of all aluminium derivatives are displayed as Figures S36–S40 in SI.

### 3.4. UV-VIS absorption investigation

Absorption spectra for the synthesized complexes were recorded in acetonitrile solvent (Figure 2). Electronic spectra of 1a, 1b, 1c, 1d and 1e display emerging peaks at 342, 327, 322, 374 and 467 nm, respectively. Aluminium derivatives 2a, 2b, 2c, 2d and 2e exhibit absorption maxima at 281, 242, 310, 284 and 378 nm, respectively. On comparing the UV-VIS spectra of ligands and complexes, peaks of the new complexes shift towards blue region as evidence for complex formation.
3.5. Stability studies

Normally, all metal alkoxides are highly moisture sensitive and must be protected from exposure to avoid formation of corresponding metal hydroxides. But, after the metal center is chelated with β-diketone and ligand moieties, the moisture sensitivity is decreased considerably because of loss of -OPri species. Thus, in order to investigate stability in the new derivatives, comparison between 1H NMR spectra of 2a was carried out in protected and exposed samples. It is important to mention that despite exposing 2a for 3 weeks, there was no sign of variation in its 1H NMR spectrum at all (Figure 3). In a similar fashion, UV–VIS investigation also revealed that there was no relocation in characteristic absorption peak at 281 nm. Further, the UV–VIS spectrum of 2a was recorded twice within 36 h while using acetonitrile as solvent; the location of the band at 281 nm remained unaltered. Therefore, the aluminium complexes could be quite stable in the ambient conditions.

3.6. Synthesis and structural characterization of nano-alumina by sol-gel technique

Despite availability of nano-alumina commercially, the newly synthesized derivative of aluminium 2a was best suited to produce high quality nano-alumina via tailor made hydrolysis. The chemical modification in the precursors alter the electronic environment, changing the kinetics of the hydrolysis process resulting in variation in the morphology of the nanostructured metal oxides. Evidently, -Br and -NO2 present in 2d and 2e, respectively, normally undergo very rapid hydrolysis followed by condensation of metal complexes. Similarly, derivatives 2b and 2c are also not appropriate to be subjected for sol-gel due to alkoxy groups -OMe and -OEt which retard the hydrolysis and condensation of the metal complexes while treating them via sol-gel technique. Thus, among the synthesized aluminium(III) derivatives, 2a was perfectly balanced to transform into corresponding nano-alumina through sol-gel route in the expected morphology and yield.
Therefore, in order to obtain nano aluminium oxide from 2a with uniform surface morphology, crystalline size and shape, it was subjected to hydrolysis by addition of distilled water and ethanol mixture (1:5) in the presence of acidic (HCl) media. The gel was not formed instantly on addition of water and ethanol mixture. Therefore, excess water was added to accelerate the hydrolysis while maintaining acidic environment. The mixture was stirred continuously for 2 days and formation of gel was observed. The obtained xerogel was preheated in hot air oven above 110°C for 24 h to yield creamy-white powder. The powder was ground and the final product was divided into 3 portions, and these portions were sintered at 800°C, 1000°C and 1200°C for 4 h. The obtained white nano-alumina was characterized by powder XRD, FTIR, TGA-DTA, Raman, BET, Fe-SEM, TEM and EDX analyses. The systematic pathway of synthesized nanostructured Al₂O₃ is exhibited in Figure 4.

3.6.1. FTIR spectra of synthesized alumina
FTIR spectrum of nano-alumina obtained by calcination at 800°C of alumina showed stretching frequencies at 3431 and 1637 cm⁻¹ which could be assigned as stretching and bending modes of water absorption and Al-OH bonds, respectively [27, 44, 45]. Similarly, nano-alumina obtained by sintering at 1000°C exhibited γ-alumina stretching bands at 1004, 799, 538 and 509 cm⁻¹ [46]. The stretching frequencies disappeared and formed new stretching frequencies at 800, 762, 629, 561, 521 and 440 cm⁻¹ due to the formation of nano crystalline α-alumina [47]. Further, subjecting nano-alumina sintering at 1200°C showed broad intense peak at 520 cm⁻¹ categorized by the presence of Al-O stretching frequency that authenticated the formation of Al₂O₃. Water
absorption peaks at 3431 and 1637 cm\(^{-1}\) have disappeared at higher calcination temperatures (1000 °C and 1200 °C) as displayed in Figure 5.

3.6.2. Powder X-ray diffraction
Powder X-ray diffraction was employed to find the average crystallite size of the nano-alumina which was calculated owing to the Debye-Scherrer equation \[ D = \frac{K\lambda}{\beta\cos\theta} \]
where D is the crystallite size, \(\kappa\) is Scherrer constant, \(\lambda\) is wavelength of X-ray, \(\beta\) is FWHM (full width half maximum) or integral breadth, \(\theta\) is Bragg angle and it was observed that the \(\alpha\)-alumina nanoparticles developed at 1200 °C possessed average size at 21 nm from powder XRD data (Figure 6) followed by the calculated values displayed in Table 2 using above-said equation and particles in the range of 9–46 nm. Different phases of synthesized alumina were determined by comparing the powder XRD diffraction patterns of obtained crystal peaks (Figure 6) with previously reported
data (standard JCPDS values). Powder XRD patterns of $\text{Al}_2\text{O}_3$ synthesized at 1200 °C showed 20 peaks at 25.70 (012), 31.50 (004), 32.92 (20–2), 35.27 (104), 36.22 (111), 37.89 (110), 38.93 (104), 39.84 (20–4), 43.48 (113), 45.07 (21–1), 52.69 (30–4), 57.63 (116) and 67.50 (215) corresponding to $\alpha$-$\text{Al}_2\text{O}_3$ (JCPDS No. 00-035-0121). Though, the relevant data for average size of crystalline alumina particles prepared at different temperatures (800 °C, 1000 °C and 1200 °C) have also been charted in Table 3.

### 3.6.3. TGA and DTA analysis

DTA plot of alumina in Figure 7 displayed minor weight loss and had two endothermic peaks located at 83 °C and 257 °C corresponding to removal of alcohol and water, respectively [48]. While increasing the temperature, numerous overlapping masses were lost and were detected on heating up to 1200 °C. At 418 °C, $\text{Al}_2\text{O}_3$ was decomposed to harvest $\gamma$-alumina associated with loss of OH and dehydration processes. Further, on increasing temperature to 1200 °C, exothermic peak was observed in DTA.
curve at 1172.33 °C that could be attributed to phase transformation of α-alumina [48].

TGA curve (Figure 7) exhibited 12.74% as first weight loss of alumina nano powder due to elimination of water and 18.56% as second weight loss from removal of hydroxy group as well as exclusion of other impurities by 600 °C. The temperature above 600 °C to 1200 °C displayed minute percentage weight loss because of higher temperature and finally different phase transformation as α-alumina [49].

Table 3. Weight loss, crystal size and phase difference at different temperatures.

| Samples | Sintering temperature (°C) | Weight (g) (before sintering) | Weight (g) (after sintering) | Weight loss (%) | Appearance       | Average crystallite size (nm) |
|---------|-----------------------------|-------------------------------|-------------------------------|----------------|------------------|-----------------------------|
| A       | 800                         | 0.3                           | 0.257                         | 14.3           | Amorphous        | 3                           |
| B       | 1000                        | 0.3                           | 0.218                         | 27.3           | Amorphous/Crystalline | 12                          |
| C       | 1200                        | 0.3                           | 0.210                         | 30             | Crystalline      | 21                          |

Figure 7. TGA and DTA plots of alumina powder.

Figure 8. Raman spectrum of α-alumina.
3.6.4. Raman spectroscopy

Raman spectrum of the sample is a fingerprint of each component in the sample. The peak intensity vs. shift (band) of Raman spectrum reflects the phase or components present in the sample. Figure 8 exhibits the various vibrational modes of \( \alpha \)-alumina nanoparticles as 374, 410, 574, 643 and 747 cm\(^{-1} \) and it verifies the alpha phase of Al\(_2\)O\(_3\) and Raman shift were in accordance with each other [50, 51].

3.6.5. BET analysis

Specific area and pore volume of alumina were carried out by using micromeritics, accelerated surface area and porosity system Quantachrome USA. All three samples were sintered at different temperatures and alumina degassed at 300 °C for 5 h prior to specific surface area measurement based on the Brunauer-Emmett-Taller (BET) principle [52]. Figure 9 displays adsorption-desorption isotherm distribution plots of alumina along with pores and porosity. It appeared to be a type IV isotherm and type H1 hysteresis loop which were recommended as mesoporous structures [29]. The calcination time and permissible temperature systematically led to the development of nano particles with high surface area and pore size of metal oxides [53]. As a result, the presence of mesoporous structures and large pore volume provide an environment for dye removal via liquid phase adsorption.

Table 4 reveals surface area and pore volume of alumina powder at different calcination temperatures. The annealed sample at 800 °C was analyzed for BET for 9 h, possessing highest surface area 1135.364 m\(^2\) g\(^{-1}\) by Barret-Joyner-Halenda (BJH) and 52.66 m\(^2\) g\(^{-1}\) by BET methods. This greater specific surface area cannot be retained at higher temperature. It is evident from the literature that surface area decreases with increase in calcination temperature above 700 °C [54, 55]. The calcinated sample at 1000 °C for 27 h resulted in 320.585 m\(^2\) g\(^{-1}\) (BJH) and 51.446 m\(^2\) g\(^{-1}\) (BET) while finally at 1200 °C the sample exhibited drastic reduction in surface area as 10.384 m\(^2\) g\(^{-1}\) (BJH) and 1.127 m\(^2\) g\(^{-1}\) (BET). Complete transformation of mixture phase into \( \alpha \)-Al\(_2\)O\(_3\) took place and surface area also shrunk as 100% \( \alpha \)-alumina formed [56].

Figure 9. N\(_2\) adsorption-desorption isotherm plot of alumina sintered at 800 °C, 1000 °C and 1200 °C.
3.6.6. Fe-SEM

Morphology and size of alumina were examined by Fe-SEM study. The Fe-SEM images of newly synthesized aluminium oxide sintered at 1200 °C exhibited 100–200 nm size due to aggregation and dispersed evenly because of higher sintering temperature as revealed in Figure 10b. Micrograph of Al₂O₃ exhibited tiny crystalline particles with variation in size and shapes. These micrograph Fe-SEM images of α-Al₂O₃ guaranteed that the particles size and crystallinity increased by increasing annealing temperature. The mapping images of alumina are displayed in Figure 10d where aluminium appeared as green in Figure 10e mapping and oxygen is reflected as red color in Figure 10f. Further, EDX image (Figure 10c) authenticates the purity and quantitative analysis of alumina where its composition with the expected signals of aluminium (54.2%) and oxygen (45.8%) are clearly visible.

3.6.7. HR-TEM

The diameter size and shape of individual ultrapure nano particles was confirmed in transmission electron microscopy (TEM) images revealed in Figure 11. Most of the particles were established as porous and aggregate network images wherein particles were agglomerated because of weakly bonded van der Waals force and aggregated due to attachment by strong chemical bonds [57]. In the present investigation, 20–80 nm aggregated particles were obtained as exhibited in Figure 11a,b with average particle size 44.5 nm. Most of the particles were observed as spherical and slit-

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**Table 4.** Surface area and pore volume of Al₂O₃ at different annealing temperatures.

| Sample code (°C) | Specific surface area (m² g⁻¹) (BJH) | Pore volume cm³/ g⁻¹ (BJH) | Mean adsorption pore diameter (nm) (BET) | Average crystallite size (nm) (P-XRD) |
|------------------|--------------------------------------|-----------------------------|------------------------------------------|--------------------------------------|
| 800              | 1135.364                             | 1.244                       | 52.666                                   | 3                                    |
| 1000             | 320.585                              | 0.562                       | 51.446                                   | 12                                   |
| 1200             | 10.384                               | 0.012                       | 1.129                                    | 21                                   |

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**Figure 10.** Fe-SEM images of α-Al₂O₃ – 1 μm (a), 500 nm (b), EDX (c), Mapping image of Al₂O₃ (d), Mapping image of Al (e) and Mapping image of O (f).
shaped aggregated particles encompassed by large pores [58, 59]. Crystalline $\alpha$-Al$_2$O$_3$ particles were confirmed by SAED and EDX as well as by indexing pattern image of PXD (hkl) as evident in Figure 11c,d exhibiting almost crystalline phase where some of them are organized in a plane [60].

3.7. Photodegradation of dyes

As an application of nano sized alumina, photodegradation was carried out for rhodamine-B and methyl orange. Decoloration of both dyes was investigated under sun-light.
Blank observation was achieved by making 100 mg/L dye aqueous solution without addition of nano-alumina [29]. The nanocrystalline alumina possesses uniform surface morphology, size, shape and positive character of metal oxides (Al$^{3+}$) that improve the adsorption rate [30]. The experiments were carried out in aqueous medium in the presence of adsorbent material at three different concentrations such as 0.03, 0.04 and 0.05 grams with catalytic amount of H$_2$O$_2$ in 50 ml dyes solution under constant stirring. The

Figure 13. Effect of dye concentrations: rhodamine-B (b); methyl orange (d).

Figure 14. UV-Visible spectra for photodegradation of rhodamine-B at various concentrations: 0.03 g (a), 0.04 g (b) and 0.05 gram (c).
reaction setup was kept in the dark for 30 minutes, then exposed to sunlight. At 20 minute intervals, 3 ml of sample solution was taken out for observation till 140 minutes. Afterwards, the remaining test samples were centrifuged at 3000 rpm for 5 min then subjected for UV-absorption spectroscopy. Figures 12–17 show results.

3.7.1. Effect of alumina (photocatalyst) dosage
Figure 12 exhibits optimization of the amount of adsorbent for photodegradation of rhodamine-B and methyl orange dyes ranging from 0.03, 0.04 and 0.05 grams were examined at constant concentration of dyes in aqueous medium (100 mg/L). Figure 14 shows the UV-Vis spectra which represent rhodamine-B photodegradation by different concentrations for 140 min. The catalytic efficiency of alumina was 75%, 87% and 93% for 0.03, 0.04 and 0.05 grams of adsorbent, respectively. Similarly, Figure 16 exhibits UV-Vis spectra of methyl orange photodegradation with 0.03, 0.04 and 0.05 grams of catalyst demonstrated 73%, 85%, 94%, respectively. Moreover, the color intensity of adsorbed solution decreased with increasing applied concentration of adsorbent [56] which has more surface area and higher catalytic performance to trap the dye molecules from aqueous medium. Herein, 93% of rhodamine-B and 94% of methyl orange underwent decolorization in 0.05 grams of catalyst during 140 min. Eventually, resulting color of adsorbent material changed from white to pink for rhodamine-B in Figure 15 while yellow for methyl orange in Figure 17.

3.7.2. Effect of dye concentrations
The removal efficacies of catalyst with different initial concentrations (20 to 60 ppm) of rhodamine B and methyl orange while fixing amount of alumina at 0.03 g are displayed in Figure 13. On increasing dye concentrations, the rates of photodegradation of rhodamine-B and methyl orange decreased from 94% to 62% during the observation time (140 min). Such observations could be attributed as higher concentrations of dyes screen the transmission of sunlight, consequently, retards the catalyst activation.

In fact, greater concentration of dyes develops shortages in active sites of photocatalyst that augments uni-layer formation on its surface and eventually attachment of dyes with the adsorbent is hindered due to repulsion between dye molecules and alumina.
3.7.3. Effect of time on photodegradation of dyes

To assess the catalytic performance of α-alumina, various concentrations during the decolorization of rhodamine-B and methyl orange by UV-Vis spectroscopy of all the samples were collected for 140 min. The characteristic absorption peaks of rhodamine-B and methyl orange are at 556 and 464 nm, respectively. But, absorption intensities of both dyes $\lambda_{\text{max}} = 556$ in Figure 14c and 464 in Figure 16c were decreased constantly from initial to final stage with increasing time interval. The maximum decoloration of dye was achieved at 140th minute in the presence of 0.05 grams of adsorbent material. Thus, synthesized nanostructured alumina could be exploited as a better...
adsorbent for photodegradation of specific dyes in reasonable time. The color intensity of adsorbed solution decreased with increase in time interval and applied concentration of the adsorbent [61].

3.7.4. Plausible mechanism for photodegradation of dyes

The nano particles of alumina provide the catalytic surface during catalytic oxidation. The decomposition of H$_2$O$_2$ on the active surface of nano-alumina occurs to produce OH$^\cdot$ free radicals. Moreover, when the H$_2$O$_2$ and OH$^\cdot$ radicals are made to react in excess, they form hydro-peroxyl radicals (HO$_2^\cdot$) with liberation of water molecules. The oxidation potential of hydro-peroxyl radicals is lower compared to OH$^\cdot$ radicals hence, it is said to be an oxidant that cannot be used in oxidative degradation of dyes, instead OH$^\cdot$ is considered to be the potential radical that is capable of oxidative degradation of dyes [27]. Further, as per the observation and discussion in the previous segment (Table 4), alumina produced herein at 800 °C calcination temperature has more active surface area and enhances photocatalytic activities of dye degradation. While carrying out the process for 140 min, both dye solutions were completely mineralized by releasing CO$_2$ and H$_2$O that authenticated the complete degradation of dyes [30]. OH$^\cdot$ radicals acted as an oxidant and increased percentages of photodegradation mechanism. Photodegradation mechanism was rectified by hydroxylation of nano-alumina particles surface in aqueous medium. The surfaces of the metal oxides achieved amphoteric nature.

The positive charge on the surface of metal oxide is electrostatically attractive to anionic dye molecules, increasing the rate of dye adsorption [62, 63]. The surface of nano materials is unsaturated to bind with other species. It is worthwhile to mention that Al$_2$O$_3$ particles synthesized by sol-gel technique with 2a as precursor have greater surface area with high adsorption capacity.

3.8. Regeneration of photocatalyst

The regeneration and reusability of any catalyst is a significant feature in its commercial applications. The photocatalytic degradations of rhodamine-B and methyl orange were examined under natural sunshine with catalytic amount of alumina as adsorbent.
After degradation, the resultant alumina powder was filtered and washed with double distilled water repeatedly. Later, the powder sample was dried at 100 °C overnight to determine the catalytic activity of $\alpha$-Al$_2$O$_3$ nanoparticles during degradation and regeneration of exhausted catalyst. Figure 18 reveals that Al$_2$O$_3$ stays effective at least for five cycles before exhibiting considerable decline in regeneration capability. Thus, prepared $\alpha$-Al$_2$O$_3$ is remarkably stable in decolorization.

4. Conclusion

The investigation carried out herein comprises five new heteroleptic homonuclear aluminium(III) complexes which were synthesized and characterized to establish plausible structures. Further, new crystalline $\alpha$-alumina nanoparticles were prepared by sol-gel method from 2a at different calcination temperatures (800 °C, 1000 °C and 1200 °C). The average crystalline size of prepared alumina was 3 nm (at 800 °C) which adsorbed rhodamine-B and methyl orange from their aqueous solutions effectively. Adsorption of dye solutions was maximized within 140 min on exposure of natural sunlight. The photodegradation of both the dyes was more than 93% within shorter span of time unlike most of the reports available. Thus, it could be a key pollution scavenger.

Acknowledgments

Sathish Thanigachalam is personally grateful to the Hon’ble management of VIT Vellore for providing him stipend as a Research Associateship.

Conflict of interest

In considered opinion of the authors, any type of “conflict of interest” is not existing at all towards the publication of the present article.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported with the “VIT Seed Grant (SG20210161)” of Vellore Institute of Technology Vellore, Tamil Nadu, India to get materialized up to this level.

ORCID

Sathish Thanigachalam http://orcid.org/0000-0001-6658-5759
Madhvesh Pathak http://orcid.org/0000-0002-7211-9698
Kulathu iyer Sathiyarayarayan http://orcid.org/0000-0003-3865-4088
References

[1] D. Jeyanthi, M. Iniya, K. Krishnaveni, D. Chellappa. RSC Adv., 3, 20984 (2013).
[2] P.A. Cameron, V.C. Gibson, C. Redshaw, J.A. Segal, M.D. Bruce, A.J.P. White, D.J. Williams. Chem. Commun., 18, 1883 (1999).
[3] P.A. Cameron, V.C. Gibson, D. Irvine. Angew. Chem., 112, 2225 (2000).
[4] S. Kaler, P. McKeown, B.D. Ward, M.D. Jones. Inorg. Chem. Front., 8, 711 (2021).
[5] V. Giri Prasanth, T. Kiran, P. Gopal Aravindan, K. Iyer Sathiyanarayanan, M. Pathak. J. Coord. Chem., 68, 2480 (2015).
[6] J. Meléndez, M. North, P. Villuendas. Chem. Commun., 18, 2577 (2009).
[7] R.K. Mehrotra, R.C. Mehrotra. Can. J. Chem., 39, 795 (1961).
[8] Y.N. Chang, P.Y. Lee, X.R. Zou, H.F. Huang, Y.W. Chen, L.C. Liang. Dalton Trans., 45, 15951 (2016).
[9] M.T. Chen, Y.Y. Chen, G.L. Li, K.W. Chou, C.H. Hu, G.C. Huang, C.T. Chen. Appl. Organomet. Chem., 4, e5464 (2020).
[10] A. Saini, V. Dhayal, D.C. Agarwal. Surf. Coat. Technol., 335, 241 (2018).
[11] J. Wei, M.N. Riffel, P.L. Diaconescu. Macromolecules, 50, 1847 (2017).
[12] R.Y. Kong, M.R. Crimmin. Dalton Trans., 50, 7810 (2021).
[13] S. Seenan, S. Kulathu Iyer. J. Photochem. Photobiol. A: Chem., 418, 113441 (2021).
[14] S. Manickam, S.K. Iyer. J. Coord. Chem., 84, 11513 (2019).
[15] A. Ohki, K. Nakayachig, K. Naka, S. Maeda. Appl. Organometal. Chem., 10, 747 (1996).
[40] M. Pathak, R. Bohra, R.C. Mehrotra, I.P. Lorenz, H. Piotrowski. Trans. Met. Chem., 28, 187 (2003).
[41] V.G. Prasanth, G. Prasad, T. Kiran, R.S. Rathore, M. Pathak, K.I. Sathiyanarayanan. J. Sol-Gel Sci. Technol., 76, 195 (2015).
[42] S. Goyal, A. Singh. Inorg. Met.-Org. Chem., 32, 1433 (2002).
[43] M. Farahmandjou, N. Golabiyan. J. Ceram. Process., 2, 1 (2015).
[44] A. Afkhami, M. Saber-Tehrani, H. Bagheri. J. Hazard. Mater., 181, 836 (2010).
[45] M. Ghorbanloo, A. Heydari, H. Yahiro. Appl Organometal Chem., 32, e3917 (2018).
[46] S. Wang, X. Li, S. Wang, Y. Li, Y. Zhai. Mater. Lett., 62, 3552 (2008).
[47] Y. Adraider, S.N. Hodgson, M.C. Sharp, Z.Y. Zhang, F. Nabhani, A. Al-Waidh, Y.X. Pang. J. Eur. Ceram. Soc., 32, 4229 (2012).
[48] S.M. Kim, J.Y. Lee, K.W. Jun, J.Y. Park, H.S. Potdar. Mater. Chem. Phys., 104, 56 (2007).
[49] M.M. Martín-Ruiz, L.A. Pérez-Maqueda, T. Cordero, V. Balek, J. Subrt, N. Murafa, J. Pascual-Cosp. Ceram. Int., 35, 2111 (2009).
[50] R. Loudon. Adv. Phys., 50, 813 (2001).
[51] F.D. Cortes-Vega, W. Yang, J. Zarate-Medina, S.R. Brankovic, J.M. Ramírez, F.C. Hernandez. CrystEngComm, 20, 3505 (2018).
[52] S. Brunauer, P.H. Emmett. J. Am. Chem. Soc., 59, 2682 (1937).
[53] Y.J. Asencios, M.R. Sun-Kou. Appl. Surf. Sci., 258, 10002 (2012).
[54] M. Rajendran, A.K. Bhattacharya. Mater. Lett., 39, 188 (1999).
[55] A.J. Perrotta. Mater. Res. Innov., 2, 33 (1998).
[56] Y.C. Lee, S.B. Wen, L. Wenglin, C.P. Lin. J. Am. Ceramic Soc., 90, 1723 (2007).
[57] J. Li, J. S. Pu, W. Cao, L. Li, R. Guo. Science., 29, 368 (2020).
[58] K. Prasad, A.K. Jha, A.R. Kulkarni. Nanoscale Res. Lett., 2, 248 (2007).
[59] G. Amini, G.D. Najafpour, S.M. Rabiee, A.A. Ghoreyshi. Chem. Eng. Technol., 10, 1708 (2013).
[60] A. López-Delgado, L. Fillali, J.A. Jiménez, S. López-Andrés. J. Sol-Gel Sci. Technol., 64, 162 (2012).
[61] N.A. Ghulam, M.N. Abbas, D.E. Sachit. Indian Chem. Eng., 62, 301 (2020).
[62] Y.M. Zheng, N. Li, W.D. Zhang. Colloids Surf. A: Physicochem. Eng. Asp., 415, 195 (2012).
[63] P. Monash, G. Pugazhenthi. Environ. Prog. Sustain. Energy., 33, 154 (2014).