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AN EFFICIENT SYNTHETIC PROCEDURE FOR THE PREPARATION OF A FULL SERIES OF MESOGENIC 4-ALKOXYBENZOIC ACID AND THEIR COPPER(II) COMPLEXES

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ABSTRACT. A full series of 4-alkoxybenzoic acid (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20) ***(1a–s)*** was synthesized using a new, efficient, and practical synthetic procedure. These compounds were reacted with copper(II) acetate to produce a new series of copper(II) complexes: bis(4-alkoxybenzoate) copper(II) complexes (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20) ***(2a–s)***. The prepared compounds were described using different technology methods, including ^{1}H NMR, ^{13}C NMR, FTIR, UV-Vis, and microelemental analysis, molar conductivity measurements. Liquid crystal behaviour of the two series of substances employing polarized optical microscopy (POM). In general, the study showed that the series of 4-alkoxybenzoic acid (alkoxy: OC_nH_{2n+1}, n = 3–18, 20) ***(1a–s)*** are mesomorphic materials and exhibit enantiotropic liquid crystal characteristics. (***1a***, ***1b***, and ***1s*** show no liquid crystal properties). Compounds ***1c–f*** showed only nematic mesophase when heated and cooled; this was explained by the texture's characteristic thread- or droplet-like appearance. The rest of the compounds ***1g*** to ***1r*** showed both of smectic and nematic mesophases during the heating and cooling process. Furthermore, the mesomorphic properties of these compounds are fully disappeared upon coordination with the copper(II) ion. Therefore, bis(4-alkoxybenzoate) copper(II) complexes (alkoxy: (OC_nH_{2n+1}), n=1–18, 20) ***(2a–s)*** displays no mesomorphic properties (simply melted to isotropic liquid).

KEY WORDS: 4-Alkoxybenzoic acid, Bis(4-alkoxybenzoate) copper(II) complexes, Liquid crystal properties, Enantiotropic liquid crystal, Mesomorphic materials

INTRODUCTION

Water repellents, or hydrophobic materials, are a class of chemicals that have little attraction to water. The hydrophobicity of these materials' is mostly caused by the presence of one or more hydrocarbon chains. These materials have demonstrated some impressive uses in the domains of material science, biology, and chemistry [1-3].

Designing new application-friendly materials is attracting increasing interest in developing systems characterized by their molecular organization. Liquid crystalline materials (mesogens and metallomesogens), colloidal materials, polymers, gels, composite materials, and hydrophobic materials are classified as soft materials with great technological importance. This type of compounds is highly attractive as functional materials in various fields such as materials science, biology, and chemistry [1-3]. Among all these materials, liquid crystalline materials uniquely provide order and motion at the molecular, supra-molecular, and macroscopic levels [4, 5]. Numerous liquid crystalline materials have been designed in recent decades since botanist and chemist Friedrich Reinitzer discovered the first liquid crystalline medium with refractive capability [6-10]. This is mainly due to the remarkable applications of these materials in technology, science, and medicine (for further details, see references [6-10] and the references cited therein). Molecularly ordered materials are attractively used in active photonics and electronics devices. Moreover, supra-molecular structures for these materials can be designed to develop such devices. Light radiation or charge transport (image components, displays, solar cells,

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data processing, and storage) as physical properties are requirements for device applications in new technology. In this context, emissive liquid crystalline materials are considered as useful materials for display applications [11]. The significant interest in liquid crystalline materials as support for the new liquid crystal display technology requires increased research with a focus on providing liquid crystal color capsule displays. These devices may exhibit some limitations, such as low energy efficiency and brightness. This is primarily due to the use of color filters and polarizers that convert a significant portion of the incident light into thermal energy [12]. Photoluminescent liquid crystalline materials can overcome this drawback.

Another family of organic molecules with a carbonyl group is carboxylic acids. They are widely found in nature and play a significant role in foods like butter, vinegar, and vegetable oils. Acidity is the primary chemical characteristic of carboxylic acids. Moreover, carboxylic acids generate a wide range of significant derivatives, such as acid halides, amides, esters, and anhydrides. A carboxyl group is the functional group of a carboxylic acid. Additionally, this group can coordinate to a variety of metal ions, producing interesting coordination complexes [13].

A numerous number of papers have been published in the last ten years detailing the liquid crystal characteristics of various chemical derivatives [8-12], and materials comprising metal, particularly those including aluminum [14], nickel [15], zinc [16], palladium [17], silver [18], iridium [19], platinum [20], gold [21], lanthanide ions [22], as well as copper [23-24].

Copper is found in most biological systems and is important for cell metabolism, being cofactor of different metalloenzymes [25]. It can have two oxidation states (+1 and +2), thus is a catalyst of redox cycles [26] producing partially reduced and reactive oxygen species (ROS). Cu(I) has an affinity for thioether and thiol groups, whereas Cu(II) coordinates preferentially the oxygen or imidazole nitrogen groups and interacts with proteins structures, regulating biochemical reactions [25] and exhibiting toxic effects at high concentrations [27]. However, being an endogenous metal, copper and its complexes are less toxic than non-endogenous metals, such as platinum. Cu(I) compounds are unstable and are less studied as antineoplastic, instead Cu(II) complexes have a great anticancer potential [28].

In 2006, Rezvani *et al.* prepared square planar copper(II) complexes based on a series of 5-((4-alkoxyphenyl)azo) salicylaldehyde (alkoxy = decyloxy, dodecyloxy, tetradecyloxy). All the prepared complexes showed an enantiotropic smectic C mesophase [29]. In 2009, Kadkin *et al.* incorporated copper(II) ion into the enaminoketone chelate core and produced new heteropolynuclear mesogenic systems [30].

Using a new, efficient, and practical synthetic procedure, we report the synthesis and liquid crystal behaviour of series of 4-alkoxybenzoic acid compounds (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20), in addition to evaluating the coordination behavior of this series of compounds toward copper(II) ion.

EXPERIMENTAL

Physical measurements

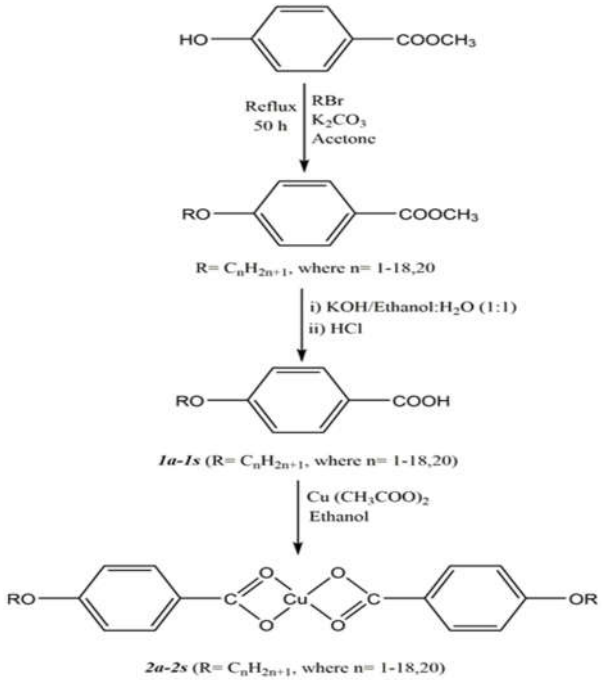
BEL Engineering UV-M90 spectrophotometer was used to record the electronic spectra of the produced compounds in the 200–800 nm range for 1×10^{-4} M in dichloromethane at room temperature. Cu was measured using a novaAA 350 flame atomic absorption spectrometer, while the elements C, H, and N were performed with a EuroEA 3000 Elemental Analyzer. ALPHA II spectrophotometer with an ATR mode was used to record the infrared spectra in the range of 4000–600 cm^{-1}. A Bruker 400 MHz ^1H NMR and 100 MHz ^{13}C NMR spectrometer was used to obtain ^1H and ^{13}C NMR spectra in $CDCl_3$. The liquid crystal mesophases of the organic compounds and their copper(II) complexes were obtained using a PW-BK5000R microscope equipped with an HS-400 (KER3100-08S) heating stage. The molar conductance of Cu(II) complexes in acetone (1×10^{-3} M) was determined at 25 °C using a DDS-307A digital conductometer.

Materials

All of the reagents used in this study were commercially and were used without further purification: 4-hydroxybenzoate (97%, Fluka Co.), methyl iodide (99%, Aldrich Co.), ethyl bromide (98%, Aldrich Co.), 1-bromopropane (97%, Aldrich Co.), 1-bromobutane (97%, CDH Co.), 1-bromopentane (97%, Aldrich Co.), hexyl bromide (99%, Aldrich Co.), heptyl bromide (98%, Aldrich Co.), 1-bromooctane (98%, Aldrich Co.), nonyl bromide (97%, Aldrich Co.), decyl bromide (97%, Aldrich Co.), 1-bromoundecane (99%, Aldrich Co.), 1-bromododecane (98%, Aldrich Co.), 1-bromotridecane (97%, Aldrich Co.), 1-bromotetrdecane (97%, Aldrich Co.), 1-bromopentadecane (95%, Aldrich Co.), 1-bromohexadecane (98%, Aldrich Co.), 1-bromoheptadecane (97%, Aldrich Co.), 1-bromooctadecane (97%, Aldrich Co.), 1-bromoicosan (97%, Aldrich Co.), potassium hydroxide (85%, SDFCL Co.), potassium carbonate (99%, Aldrich Co.).

*General procedure for the synthesis of 4-alkoxybenzoic acid (**1a–s**)*

A slurry of potassium carbonate (130 g) in acetone (250 mL) was refluxed for 50 hours with 4-hydroxybenzoate (25 g, 150 mmol) and n-alkyl halide (150 mmol) (methyl iodide was employed in the synthesis of ***1a***, whereas n-alkyl bromide was utilized in the synthesis of compounds (***1b–s***)). After filtering out the inorganic salts, the filtrate was evaporated to dryness . Then, a solution of potassium hydroxide (8.4 g in a mixture of water/ethanol (100 mL/100 mL)) was added to the residue of crude ester, and the mixture was refluxed for 24 h. Afterwards 6 mL of aqueous HCl (37%) was added to the mixture and refluxing was continued for two hours. The obtained white precipitate was filtered off and washed several times with water and two times with ethanol. Using n-hexane and ethyl acetate (3:1) as an eluent, thin layer chromatography (TLC) was used to verify the purity of the final product as shown in Scheme 1.



Scheme 1. Synthetic diagram for the preparation of compounds (**1a-s**).

*4-Methoxybenzoic acid (**1a**)*. Yield = 70%. The elemental analysis (%) calc.: C 63.15, H 5.26; found: C 62.8, H 5.11. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2916 (w, υ_{as}(C–H) of CH_3 group), 2849 (w, υ_s(C–H) of CH_3 group), 3070 (w, υ(C–H)aromatic), 1670 (s, υ(C=O)), 1599, 1575, and 1510 (s, m, m, υ(C=C)aromatic), 1255 (s, υ(C–O)), 1460 (m, δ(C–H). UV-Vis (λ/nm): 230 (n–σ*), 257 (π–π*), 280 (n–π*). ^{1}H NMR (δ/ppm): 3.73 (**3**H, t, OCH_3), 6.97 (**2**H, d, J = 8.8 Hz, aromatic protons), 7.80 (**2**H, d, J = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 56.11 (OCH_3), 114.20 (aromatic C–H), 126.87 (aromatic C), 130.02 (aromatic C–H), 162.30 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Ethoxybenzoic acid (**1b**)*. Yield = 77%. The elemental analysis (%) calc.: C 65.06 H 6.02; found: C 65.00, H 5.90. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2981 (w, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 3072 (w, υ(C–H) aromatic), 1676 (s, υ(C=O)), 1596, 1575 and 1508 (s, m, m, υ(C=C)aromatic), 1251 (s, υ(C–O)), 1475 (m, δ(C–H)). UV-Vis (λ/nm): 232 (n–σ*), 310 (π –π*), 280 (n–π*). ^{1}H NMR (δ/ppm): 1.45 (3H, t, -OCH_2**CH_3**), 4.11 (2H, q, J = 4.0, -**OCH_2**CH_3), 6.96 (2H, d, J = 9.1 Hz, aromatic protons), 7.78 (2H, d, J = 9.1 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.65 (-OCH_2**CH_3**), 63.64 (**OCH_2**CH_3), 114.84 (aromatic C–H), 127.11 (aromatic C), 130.05 (aromatic C–H), 161.44 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Proryloxybenzoic acid (**1c**)*. Yield = 60%. The elemental analysis (%) calc.: C 66.66, H 6.66; found: C 66.18, H 6.38. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2966 (w, υ_{as}(C–H) of CH_3 group), 2877 (w, υ_s(C–H) of CH_3 group), 2935 (m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H)aromatic), 1687 (s, υ(C=O)), 1597, 1575, and 1508 (s, m, m, υ(C=C)aromatic), 1253 (s, υ(C–O)), 1471 (m, δ(C–H)). UV-Vis (λ/nm): 242 (n–σ*), 256 (π–π*), 284 (n–π*). ^{1}H NMR (*δ*/ppm): 1.08 (3H, t, -OCH_2CH_2**CH_3**), 1.85 (2H, m, -OCH_2**CH_2**CH_3), 4.00 (2H, t, -**OCH_2**CH_2CH_3), 6.97 (2H, d, J = 8.8 Hz, aromatic protons), 7.79 (2H, d, J = 9.1 Hz, aromatic protons).^{13}C NMR (*δ*/ppm): 10.52 (-OCH_2CH_2**CH_3**), 22.54 (-OCH_2**CH_2**CH_3), 69.64 (-**OCH_2**CH_2CH_3), 114.75 (aromatic C–H), 126.80 (aromatic C), 130.12 (aromatic C–H), 161.62 (aromatic **C**–OCH_2), 175.25 (C=O).

*4-Butyloxybenzoic acid (**1d**)*. Yield = 80%. The elemental analysis (%) calc.: C 68.04, H 7.21; found: C 67.9, H 7.00. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2976 (w, υ_{as}(C–H) of CH_3 group), 2938 (w-m, υ_s(C–H) of CH_3 group), 2959 (m, υ_{as}(C–H) of CH_2 group), 2872 (w, υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H)aromatic), 1688 (s, υ(C=O)), 1599, 1575, and 1508 (s, m, m, υ(C=C) aromatic), 1252 (s, υ(C–O)), 1468(m, δ(C–H)). UV-Vis (λ/nm): 241 (n–σ*), 259 (π–π*), 280 (n–π*). ^{1}H NMR (δ/ppm): 0.97 (3H, t, -$OCH_2(CH_2)_2$**CH_3**), 1.41 (2H, m, -OCH_2CH_2**CH_2**CH_3), 1.85 (2H, m, -OCH_2**CH_2**CH_2CH_3), 4.01 (2H, t, -**OCH_2**$(CH_2)_2CH_3$), 6.93 (2H, d, J = 9.0 Hz, aromatic protons), 7.75 (2H, d, J = 9.0 Hz, aromatic protons), ^{13}C NMR (δ/ppm): 14.41 (-$OCH_2(CH_2)_2$**CH_3**), 21.40 (-OCH_2CH_2**CH_2**CH_3), 30.84 (-OCH_2**CH_2**CH_2CH_3) 68.94 (-**OCH_2**$(CH_2)_2CH_3$), 114.30 (aromatic C–H), 127.20 (aromatic C), 130.33 (aromatic C–H), 161.72 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Pentyloxybenzoic acid (**1e**)*. Yield = 67%. The elemental analysis (%) calc.: C 69.23, H 7.69; found: C 68.9, H 7.4. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2933 (m, υ_{as}(C–H) of CH_2 group), 2862 (m, υ_s(C– H) of CH_2 group), 3070 (w, υ(C–H) aromatic), 1687 (s, υ(C=O)), 1599, 1577, and 1508 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1467 (m, δ(C–H)). UV-Vis (λ/nm): 235 (n–σ*), 259 (π–π*), 270 (n–π*). ^{1}H NMR (δ/ppm): 0.97 (3H, t, -$OCH_2(CH_2)_3$**CH_3**), 1.27–1.55 (4H, m, -OCH_2CH_2**$(CH_2)_2$**CH_3), 1.84 (2H, m, -OCH_2**CH_2**$(CH_2)_2CH_3$), 4.02 (2H, t, -**OCH_2**$(CH_2)_3CH_3$), 6.97 (2H, d, J = 9.1 Hz, aromatic protons), 7.80 (2H, d, J = 9.1 Hz, aromatic protons), ^{13}C NMR (δ/ppm): 14.04 (-$OCH_2(CH_2)_3$**CH_3**), 22.48 (-$OCH_2(CH_2)_2$**CH_2**CH_3), 28.19 (-OCH_2CH_2**CH_2**CH_2CH_3), 28.90 (-OCH_2**CH_2**$(CH_2)_2CH_3$), 68.15 (-**OCH_2**$(CH_2)_3CH_3$), 114.76

(aromatic C–H), 126.79 (aromatic C),130.13 (aromatic C–H), 161.64 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Hexyloxybenzoic acid (**1f**)*. Yield = 65%. The elemental analysis (%) calc.: C 76.4, H 8.9; found: C 76.3, H8.8. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w-m, υ_{as}(C–H) of CH_3 group), 2870 (w, υ_s(C–H) of CH_3 group), 2930 (m, υ_{as}(C–H) of CH_2 group), 2859 (m, υ_s(C–H) of CH_2 group), 3073 (w, υ(C–H) aromatic), 1692 (s, υ(C=O)), 1599, 1576, and 1508 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1470(m, δ(C–H)). UV-Vis (λ/nm): 229 (n–σ^*), 245 (π–π^*), 280 (n–π^*). ^{1}H NMR (δ/ppm): 0.90 (3H, t, -$OCH_2(CH_2)_4$**CH_3**), 1.37–1.46 (6H, m, -OCH_2CH_2**$(CH_2)_3$**CH_3), 1.84 (2H, m, -OCH_2**CH_2**$(CH_2)_3CH_3$), 4.0 (2H, t, -**OCH_2**$(CH_2)_4CH_3$), 6.94 (2H, d, *J* = 8.9 Hz, aromatic protons), 7.76 (2H, d, *J* = 8.8 Hz, aromatic protons), ^{13}C NMR (δ/ppm): 14.16 (-$OCH_2(CH_2)_4$**CH_3**), 22.72 (-$OCH_2(CH_2)_3$**CH_2**CH_3), 25.82 (-$OCH_2(CH_2)_2$**CH_2**CH_2CH_3), 29.28 (-OCH_2CH_2**CH_2**$(CH_2)_2CH_3$), 31.70 (-OCH_2**CH_2**$(CH_2)_3CH_3$), 68.28 (-**OCH_2**$(CH_2)_4CH_3$), 114.86 (aromatic C–H), 126.91 (aromatic C), 130.22 (aromatic C–H), 161.74 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Heptyloxybenzoic acid (**1g**)*. Yield = 70%. The elemental analysis (%) calc.: C 71.11, H 8.47; found: C 71.1, H 8.2. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2956 (w-m, υ_{as}(C–H) of CH_3 group), 2867 (w, υ_s(C–H) of CH_3 group), 2928 (m, υ_{as}(C–H) of CH_2 group), 2857 (m, υ_s(C–H) of CH_2 group), 3075 (w, υ(C–H)aromatic), 1692 (s, υ(C=O)), 1599, 1576, and 1508 (s, m, m, υ(C=C) aromatic), 1254 (s, υ(C–O)), 1468 (m, δ(C–H)). UV-Vis (λ/nm): 239 (n–σ^*), 255 (π–π^*), 285 (n–π^*). ^{1}H NMR (δ/ppm): 0.96 (3H, t, -$OCH_2(CH_2)_5$**CH_3**), 1.29–1.49 (8H, m, -OCH_2CH_2**$(CH_2)_4$**CH_3), 1.83 (2H, m, -OCH_2**CH_2**$(CH_2)_4CH_3$), 4.0 (2H, t, -**OCH_2**$(CH_2)_5CH_3$), 6.94 (2H, d, *J* = 8.9 Hz, aromatic protons), 7.81 (2H, d, *J* = 8.9 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.01 (-$OCH_2(CH_2)_5$**CH_3**), 23.10 (-$OCH_2(CH_2)_4$**CH_2**CH_3), 26.60 (-$OCH_2(CH_2)_3$**CH_2**CH_2CH_3), 30.0 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_2CH_3$), 32.50 (-OCH_2CH_2**CH_2**$(CH_2)_3CH_3$), 32.70 (-OCH_2**CH_2**$(CH_2)_4CH_3$), 69.11 (-**OCH_2**$(CH_2)_5CH_3$), 114.30 (aromatic C–H), 127.21 (aromatic C), 130.02 (aromatic C–H), 161.66 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Octyloxybenzoic acid (**1h**)*. Yield = 77%. The elemental analysis (%) calc.: C 72.00, H 8.80; found: C 71.94, H 8.4. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w-m, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2926 (m, υ_{as}(C–H) of CH_2 group), 2855 (m, υ_s(C–H) of CH_2 group), 3073 (w, υ(C–H)aromatic), 1692 (s, υ(C=O)), 1599, 1576, and 1508 (s, m, m, υ(C=C)aromatic), 1254 (s, υ(C–O)), 1468 (m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ^*), 255 (π–π^*), 277 (n–π^*). ^{1}H NMR (δ/ppm): 0.90 (3H, t, -$OCH_2(CH_2)_6$**CH_3**), 1.28–1.45 (10H, m, -OCH_2CH_2**$(CH_2)_5$**CH_3), 1.84 (2H, m, -OCH_2**CH_2**$(CH_2)_5CH_3$), 4.0 (2H, t, -**OCH_2**$(CH_2)_6CH_3$), 6.95 (2H, d, *J* = 8.8 Hz, aromatic protons), 7.80 (4H, d, *J* = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.24 (-$OCH_2(CH_2)_6$**CH_3**), 22.79 (-$OCH_2(CH_2)_5$**CH_2**CH_3), 26.15 (-$OCH_2(CH_2)_4$**CH_2**CH_2CH_3), 29.32 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_2CH_3$), 29.48 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_3CH_3$), 31.95 (-OCH_2CH_2**CH_2**$(CH_2)_4CH_3$), 32.50 (-OCH_2**CH_2**$(CH_2)_5CH_3$) 68.29 (-**OCH_2**$(CH_2)_6CH_3$), 114.87 (aromatic C–H), 126.91 (aromatic C), 130.22 (aromatic C–H), 161.74 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Nonyloxybenzoic acid (**1i**)*. Yield = 75%. The elemental analysis (%) calc.: C 78.0, H 9.8; found: C 77.8, H 9.7. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2952 (w, υ_{as}(C–H) of CH_3 group), 2870 (w, υ_s(C–H) of CH_3 group), 2926 (s, υ_{as}(C–H) of CH_2 group), 2852 (m, υ_s(C–H) of CH_2 group), 3074 (w, υ(C–H)aromatic), 1693 (s, υ(C=O)), 1599, 1575, and 1508 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1467 (m, δ(C–H)). UV-Vis (λ/nm): 227 (n–σ^*), 257 (π–π^*), 280 (n–π^*). ^{1}H NMR (δ/ppm): 0.91 (3H, t, -$OCH_2(CH_2)_7$**CH_3**), 1.31–1.49 (12H, m, -OCH_2CH_2**$(CH_2)_6$**CH_3), 1.83 (2H, m, -OCH_2**CH_2**$(CH_2)_6CH_3$), 4.03 (2H, t, -**OCH_2**$(CH_2)_7CH_3$), 6.97 (2H, d, *J* = 8.8 Hz, aromatic protons), 7.79 (2H, d, *J* = 8.8 Hz, aromatic protons). ^{13}C NMR

(δ/ppm): 14.13 (-$OCH_2(CH_2)_7$**CH_3**), 22.69 (-$OCH_2(CH_2)_6$**CH_2**CH_3), 26.03 (-$OCH_2(CH_2)_5$**CH_2**CH_2CH_3), 29.28 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_2CH_3$), 29.54 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_3CH_3$), 31.89 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_4CH_3$), 31.90 (-OCH_2CH_2**CH_2** $(CH_2)_5CH_3$), 32.30 (-OCH_2**CH_2**$(CH_2)_6CH_3$), 68.19 (-**OCH_2**$(CH_2)_7CH_3$), 114.76 (aromatic C–H), 126.73 (aromatic C), 130.14(aromatic C–H), , 161.67 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Decyloxybenzoic acid (**1j**)*. Yield = 70%. The elemental analysis (%) calc.: C 73.43, H 9.35; found: C 73.1, H 9.1. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2956 (w, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2923 (s, υ_{as}(C–H) of CH_2 group), 2852 (m, υ_s(C–H) of CH_2 group), 3075 (w, υ(C–H)aromatic), 1694 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1251 (s, υ(C–O)), 1463 (m, δ(C–H)). UV-Vis (λ/nm): 234 (n–σ^*), 257 (π–π^*), 284 (n–π^*). ^{1}H NMR (δ/ppm): 0.98 (3H, t, -$OCH_2(CH_2)_8$**CH_3**), 1.30–1.48 (14H, m, -OCH_2CH_2**$(CH_2)_7$**CH_3), 1.81 (2H, m, -OCH_2**CH_2**$(CH_2)_7CH_3$), 4.03 (2H, t, -**OCH_2**$(CH_2)_8CH_3$), 6.95 (2H, d, J = 8.9 Hz, aromatic protons), 7.80 (2H, d, J = 8.9 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.07 (-$OCH_2(CH_2)_8$**CH_3**), 23.28 (-$OCH_2(CH_2)_7$**CH_2**CH_3), 26.66 (-$OCH_2(CH_2)_6$**CH_2**CH_2CH_3), 29.47 (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_2CH_3$), 30.14 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_3CH_3$), 31.94 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_4CH_3$), 32.10 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_5CH_3$) 32.30 (-OCH_2CH_2**CH_2**$(CH_2)_6CH_3$), 32.50 (-OCH_2**CH_2**$(CH_2)_7CH_3$), 68.08 (-**OCH_2**$(CH_2)_8CH_3$), 114.44 (aromatic C–H), 126.89 (aromatic C), 129.81 (aromatic C–H), 161.69 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Undecyloxybenzoic acid (**1k**)*. Yield = 75%. The elemental analysis (%) calc.: C 73.97, H 9.58; found: C 73.1, H 9.1. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2956 (w, υ_{as}(C–H) of CH_3 group), 2869 (w, υ_s(C–H) of CH_3 group), 2923 (s, υ_{as}(C–H) of CH_2 group), 2852 (m, υ_s(C–H) of CH_2 group), 3075 (w, υ(C–H)aromatic), 1694 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1251 (s, υ(C–O)), 1463 (m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ^*), 250 (π–π^*), 275 (n–π^*). ^{1}H NMR (δ/ppm): 0.98 (3H, t, -$OCH_2(CH_2)_9$**CH_3**), 1.30–1.48 (16H, m, -OCH_2CH_2**$(CH_2)_8$**CH_3), 1.81 (2H, m, -OCH_2**CH_2**$(CH_2)_8CH_3$), 4.03 (2H, t, -**OCH_2**$(CH_2)_9CH_3$), 6.95 (2H, d, J = 8.9 Hz, aromatic protons), 7.80 (2H, d, J = 8.9 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.07 (-$OCH_2(CH_2)_9$**CH_3**), 23.28 (-$OCH_2(CH_2)_8$**CH_2**CH_3), 26.66 (-$OCH_2(CH_2)_7$**CH_2**CH_2CH_3), 29.47 (-$OCH_2(CH_2)_6$**CH_2**$(CH_2)_2CH_3$), 30.14 (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_3CH_3$), 31.94 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_4CH_3$), 32.10 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_5CH_3$), 32.22 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_6CH_3$), 32.30 (-OCH_2CH_2**CH_2**$(CH_2)_7CH_3$), 32.50 (-OCH_2**CH_2**$(CH_2)_8CH_3$), 68.08 (-**OCH_2**$(CH_2)_9CH_3$), 114.44 (aromatic C–H), 126.89 (aromatic C), 129.81 (aromatic C–H), 161.69 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Dodecyloxybenzoic acid (**1l**)*. Yield = 88%. The elemental analysis (%) calc.: C 74.5, H 9.8; found: C 73.96, H 10.3. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2927 (s, υ_{as}(C–H) of CH_2 group), 2850 (m, υ_s(C–H) of CH_2 group), 3060 (w, υ(C–H)aromatic), 1693 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1463 (m, δ(C–H)). UV-Vis (λ/nm): 228 (n–σ^*), 259 (π–π^*), 280 (n–π^*). ^{1}H NMR (δ/ppm): 0.97 (3H, t, -$OCH_2(CH_2)_{10}$**CH_3**), 1.29–1.45 (18H, m, -OCH_2CH_2**$(CH_2)_9$**CH_3), 1.80 (2H, m, -OCH_2**CH_2**$(CH_2)_9CH_3$), 4.02 (2H, t, -**OCH_2**$(CH_2)_{10}CH_3$), 6.94 (2H, d, J = 8.8 Hz, aromatic protons), 7.81 (2H, d, J = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.11 (-$OCH_2(CH_2)_{10}$**CH_3**), 22.96 (-$OCH_2(CH_2)_9$**CH_2**CH_3), 25.99 (-$OCH_2(CH_2)_8$**CH_2**CH_2CH_3), 29.11 (-$OCH_2(CH_2)_7$**CH_2**$(CH_2)_2CH_3$), 29.11 (-$OCH_2(CH_2)_6$**CH_2**$(CH_2)_3CH_3$), 29.35 (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_4CH_3$), 29.56 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_5CH_3$), 29.59 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_6CH_3$), 29.64 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_7CH_3$), 29.67 (-OCH_2CH_2**CH_2**$(CH_2)_8CH_3$), 31.93 (-OCH_2**CH_2**$(CH_2)_9CH_3$), 68.32 (-**OCH_2**$(CH_2)_{10}CH_3$), 114.22 ((C–H) aromatic), 121.42 ((C) aromatic), 132.35 ((C–H) aromatic), 163.73 ((**C**–OCH_2) aromatic), 172.03 (C=O).

*4-Tridecyloxybenzoic acid (**1m**)*. Yield = 75%. The elemental analysis (%) calc.: C 75.0, H 10.0; found: C 74.90, H 10.4. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2927 (s, υ_{as}(C–H) of CH_2 group), 2850 (m, υ_s(C–H) of CH_2 group), 3060 (w, υ(C–H)aromatic), 1693 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1463 (m, δ(C–H)). UV-Vis (λ/nm): 228 (n–σ), 259 (π–π), 288 (n–π). ^{1}H NMR (δ/ppm): 0.97 (3H, t, -$OCH_2(CH_2)_{11}$**CH_3**), 1.29–1.45 (20H, m, -OCH_2CH_2**$(CH_2)_{10}$**CH_3), 1.80 (2H, m, -OCH_2**CH_2**$(CH_2)_{10}CH_3$), 4.02 (2H, t, -**OCH_2**$(CH_2)_{11}CH_3$), 6.94 (2H, d, J = 8.8 Hz, aromatic protons), 7.81 (2H, d, J = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.05 (-$OCH_2(CH_2)_{11}$**CH_3**), 23.25 (-$OCH_2(CH_2)_{10}$**CH_2**CH_3), 26.69 (-$OCH_2(CH_2)_9$**CH_2**CH_2CH_3), 29.44 (-$OCH_2(CH_2)_8$**CH_2**$(CH_2)_2CH_3$), 30.11 (-$OCH_2(CH_2)_7$**CH_2**$(CH_2)_3CH_3$), 31.92 (-$OCH_2(CH_2)_6$**CH_2**$(CH_2)_4CH_3$), (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_5CH_3$), 31.93 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_6CH_3$), 31.95 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_7CH_3$), 32.03 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_8CH_3$), 32.10 (-OCH_2CH_2**CH_2**$(CH_2)_9CH_3$), 32.13 (-OCH_2**CH_2**$(CH_2)_{10}CH_3$), 68.07 (-**OCH_2**$(CH_2)_{11}CH_3$), 114.41 (aromatic C–H), 126.89 (aromatic C), 129.79 (aromatic C–H), 161.61 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Tetradecyloxybenzoic acid (**1n**)*. Yield = 73%. The elemental analysis (%) calc.: C 75.44, H 10.17; found: C 75.0, H 9.94. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2927 (s, υ_{as}(C–H) of CH_2 group), 2850 (m, υ_s(C–H) of CH_2 group), 3060 (w, υ(C–H)aromatic), 1693 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1463 (m, δ(C–H)). UV-Vis (λ/nm): 223 (n–σ^*), 249 (π–π^*), 285 (n–π^*). ^{1}H NMR (δ/ppm): 0.97 (3H, t, -$OCH_2(CH_2)_{12}$**CH_3**), 1.29–1.45 (22H, m, -OCH_2CH_2**$(CH_2)_{11}$**CH_3), 1.80 (2H, m, -OCH_2**CH_2**$(CH_2)_{11}CH_3$), 4.02 (2H, t, -**OCH_2**$(CH_2)_{12}CH_3$), 6.94 (2H, d, J = 8.8 Hz, aromatic protons), 7.81 (2H, d, J = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.05 (-$OCH_2(CH_2)_{12}$**CH_3**), 23.25 (-$OCH_2(CH_2)_{11}$**CH_2**CH_3), 26.69 (-$OCH_2(CH_2)_{10}$**CH_2**CH_2CH_3), 29.44 (-$OCH_2(CH_2)_9$**CH_2**$(CH_2)_2CH_3$), 30.11 (-$OCH_2(CH_2)_8$**CH_2**$(CH_2)_3CH_3$), 30.66 (-$OCH_2(CH_2)_7$**CH_2**$(CH_2)_4CH_3$), 30.81 (-$OCH_2(CH_2)_6$**CH_2**$(CH_2)_5CH_3$), 31.22 (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_6CH_3$), 31.79 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_7CH_3$), 31.95 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_8CH_3$), 32.03 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_9CH_3$), 32.10 (-OCH_2CH_2**CH_2**$(CH_2)_{10}CH_3$), 32.13 (-OCH_2**CH_2**$(CH_2)_{11}CH_3$), 68.07 (-**OCH_2**$(CH_2)_{12}CH_3$), 114.41 (aromatic C–H), 126.89 (aromatic C), 129.79 (aromatic C–H), 161.61 (aromatic **C**–OCH_2), 172.03 (C=O).

*4-Pentadecyloxybenzoic acid (**1o**)*. Yield = 73%. The elemental analysis (%) calc.: C 75.86, H 10.34; found: C 75.0, H 10.4. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2953 (w, υ_{as}(C–H) of CH_3 group), 2872 (w, υ_s(C–H) of CH_3 group), 2927 (s, υ_{as}(C–H) of CH_2 group), 2850 (m, υ_s(C–H) of CH_2 group), 3060 (w, υ(C–H)aromatic), 1693 (s, υ(C=O)), 1599, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1252 (s, υ(C–O)), 1463 (m, δ(C–H)). UV-Vis (λ/nm): 229 (n–σ*), 257 (π–π*), 285 (n–π*). ^{1}H NMR (δ/ppm): 0.93 (3H, t, -$OCH_2(CH_2)_{13}$**CH_3**), 1.31–1.46 (24H, m, -OCH_2CH_2**$(CH_2)_{12}$**CH_3), 1.81 (2H, m, -OCH_2**CH_2**$(CH_2)_{12}CH_3$), 4.03 (2H, t, -**OCH_2**$(CH_2)_{13}CH_3$), 6.92 (2H, d, J = 8.9 Hz, aromatic protons), 7.83 (2H, d, J = 8.9 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.08 (-$OCH_2(CH_2)_{13}$**CH_3**), 23.21 (-$OCH_2(CH_2)_{12}$**CH_2**CH_3), 26.55 (-$OCH_2(CH_2)_{11}$**CH_2**CH_2CH_3), 29.49 (-$OCH_2(CH_2)_{10}$**CH_2**$(CH_2)_2CH_3$), 30.16 (-$OCH_2(CH_2)_9$**CH_2**$(CH_2)_3CH_3$), 30.67 (-$OCH_2(CH_2)_8$**CH_2**$(CH_2)_4CH_3$), 30.89 (-$OCH_2(CH_2)_7$**CH_2**$(CH_2)_5CH_3$), 31.19 (-$OCH_2(CH_2)_6$**CH_2**$(CH_2)_6CH_3$), 31.72 (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_7CH_3$), 31.98 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_8CH_3$), 32.08 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_9CH_3$), 32.08 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_9CH_3$), 32.15 (-OCH_2CH_2**CH_2**$(CH_2)_{11}CH_3$), 32.29 (-OCH_2**CH_2**$(CH_2)_{12}CH_3$), 68.12 (-**OCH_2**$(CH_2)_{13}CH_3$), 114.41 (aromatic C–H), 126.63 (aromatic C), 129.71 (aromatic C–H), 161.65 (aromatic **C**–OCH_2), 172.12 (C=O).

*4-Hexadecyloxybenzoic acid (**1p**)*. Yield = 89%. The elemental analysis (%) calc.: C 76.24, H 10.49; found: C 76.0, H10.1. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2948 (w, υ_{as}(C–H) of CH_3 group), 2868 (w, υ_s(C–H) of CH_3 group), 2916 (s, υ_{as}(C–H) of CH_2 group), 2849 (s, υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H)aromatic), 1688 (s, υ(C=O)), 1601, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1250 (s, υ(C–O)), 1471 (m, δ(C–H)). UV-Vis (λ/nm): 231 (n–σ*), 256 (π–π*), 291 (n–π*). ^{1}H NMR (δ/ppm): 0.91 (3H, t, -$OCH_2(CH_2)_{14}\mathbf{CH_3}$), 1.33–1.48 (26H, m, -$OCH_2CH_2\mathbf{(CH_2)_{13}}CH_3$), 1.80 (2H, m, -$OCH_2\mathbf{CH_2}(CH_2)_{13}CH_3$), 4.06 (2H, t, -$\mathbf{OCH_2}(CH_2)_{14}CH_3$), 6.99 (2H, d, J = 8.7 Hz, aromatic protons), 7.82 (2H, d, J = 8.7 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.11 (-$OCH_2(CH_2)_{14}\mathbf{CH_3}$), 23.18 (-$OCH_2(CH_2)_{13}\mathbf{CH_2}CH_3$), 26.52 (-$OCH_2(CH_2)_{12}\mathbf{CH_2}CH_2CH_3$), 29.43 (-$OCH_2(CH_2)_{11}\mathbf{CH_2}(CH_2)_2CH_3$), 30.10 (-$OCH_2(CH_2)_{10}\mathbf{CH_2}(CH_2)_3CH_3$), 30.61 (-$OCH_2(CH_2)_9\mathbf{CH_2}(CH_2)_4CH_3$), 30.84 (-$OCH_2(CH_2)_8\mathbf{CH_2}(CH_2)_5CH_3$), 31.12 (-$OCH_2(CH_2)_7\mathbf{CH_2}(CH_2)_6CH_3$), 31.75 (-$OCH_2(CH_2)_6\mathbf{CH_2}(CH_2)_7CH_3$), 31.97 (-$OCH_2(CH_2)_5\mathbf{CH_2}(CH_2)_8CH_3$), 32.03 (-$OCH_2(CH_2)_4\mathbf{CH_2}(CH_2)_9CH_3$), 32.15 (-$OCH_2(CH_2)_3\mathbf{CH_2}(CH_2)_{10}CH_3$), 32.22 (-$OCH_2(CH_2)_2\mathbf{CH_2}(CH_2)_{11}CH_3$), 32.28 (-$OCH_2CH_2\mathbf{CH_2}(CH_2)_{12}CH_3$), 32.32 (-$OCH_2\mathbf{CH_2}(CH_2)_{13}CH_3$), 68.15 (-$\mathbf{OCH_2}(CH_2)_{14}CH_3$), 114.43 (aromatic C–H), 126.65 (aromatic C), 129.74 (aromatic C–H), 161.66 (aromatic **C**–OCH_2), 172.19 (C=O).

*4-Heptadecyloxybenzoic acid (**1q**)*. Yield = 89%. The elemental analysis (%) calc.: C 76.59, H 10.63; found: C 76.0, H 10.21. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2948 (w, υ_{as}(C–H) of CH_3 group), 2868 (w, υ_s(C–H) of CH_3 group), 2916 (s, υ_{as}(C–H) of CH_2 group), 2849 (s, υ_s(C–H) of CH_2 group), 3076 (w, υ(C–H)aromatic), 1688 (s, υ(C=O)), 1601, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1250 (s, υ(C–O)), 1471 (m, δ(C–H)). UV-Vis (λ/nm): 232 (n–σ*), 251 (π–π*), 293 (n–π*). ^{1}H NMR (δ/ppm): 0.93 (3H, t, -$OCH_2(CH_2)_{15}\mathbf{CH_3}$), 1.35–1.47 (28H, m, -$OCH_2CH_2\mathbf{(CH_2)_{14}}CH_3$), 1.83 (2H, m, -$OCH_2\mathbf{CH_2}(CH_2)_{14}CH_3$), 4.09 (2H, t, -$\mathbf{OCH_2}(CH_2)_{15}CH_3$), 6.98 (2H, d, J = 8.9 Hz, aromatic protons), 7.83 (2H, d, J = 8.9 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.14 (-$OCH_2(CH_2)_{15}\mathbf{CH_3}$), 23.19 (-$OCH_2(CH_2)_{14}\mathbf{CH_2}CH_3$), 26.54 (-$OCH_2(CH_2)_{13}\mathbf{CH_2}CH_2CH_3$), 29.45 (-$OCH_2(CH_2)_{12}\mathbf{CH_2}(CH_2)_2CH_3$), 30.11 (-$OCH_2(CH_2)_{11}\mathbf{CH_2}(CH_2)_3CH_3$), 30.64 (-$OCH_2(CH_2)_{10}\mathbf{CH_2}(CH_2)_4CH_3$), 30.83 (-$OCH_2(CH_2)_9\mathbf{CH_2}(CH_2)_5CH_3$), 31.11 (-$OCH_2(CH_2)_8\mathbf{CH_2}(CH_2)_6CH_3$), 31.71 (-$OCH_2(CH_2)_7\mathbf{CH_2}(CH_2)_7CH_3$), 31.98 (-$OCH_2(CH_2)_6\mathbf{CH_2}(CH_2)_8CH_3$), 32.13 (-$OCH_2(CH_2)_5\mathbf{CH_2}(CH_2)_9CH_3$), 32.19 (-$OCH_2(CH_2)_4\mathbf{CH_2}(CH_2)_{10}CH_3$), 32.29 (-$OCH_2(CH_2)_3\mathbf{CH_2}(CH_2)_{11}CH_3$), 32.38 (-$OCH_2(CH_2)_2\mathbf{CH_2}(CH_2)_{12}CH_3$), 32.41 (-$OCH_2CH_2\mathbf{CH_2}(CH_2)_{13}CH_3$), 32.45 (-$OCH_2\mathbf{CH_2}(CH_2)_{14}CH_3$), 68.12 (-$\mathbf{OCH_2}(CH_2)_{15}CH_3$), 114.42 (aromatic C–H), 126.66 (aromatic C), 129.71 (aromatic C–H), 161.63 (aromatic **C**–OCH_2), 172.17 (C=O).

*4-Octaadecyloxybenzoic acid (**1r**)*. Yield = 79%. The elemental analysis (%) calc.: C 76.92, H 10.76; found: C 76.5, H 10.3. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2960 (w, υ_{as}(C–H) of CH_3 group), 2864 (w, υ_s(C–H) of CH_3 group), 2914 (s, υ_{as}(C–H) of CH_2 group), 2850 (s, υ_s(C–H) of CH_2 group), 3064 (w, υ(C–H)aromatic), 1692 (s, υ(C=O)), 1601, 1576, and 1507 (s, m, m, υ(C=C)aromatic),1254 (s, υ(C–O)), 1470 (m, δ(C–H)). UV-Vis (λ/nm): 231 (n–σ*), 253 (π–π*), 295 (n–π*). ^{1}H NMR (δ/ppm): 0.92 (3H, t, -$OCH_2(CH_2)_{16}\mathbf{CH_3}$), 1.32–1.45 (30H, m, -$OCH_2CH_2\mathbf{(CH_2)_{15}}CH_3$), 1.82 (2H, m, -$OCH_2\mathbf{CH_2}(CH_2)_{15}CH_3$), 4.07 (2H, t, -$\mathbf{OCH_2}(CH_2)_{16}CH_3$), 6.95 (2H, d, J = 8.8 Hz, aromatic protons), 7.85 (2H, d, J = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.12 (-$OCH_2(CH_2)_{16}\mathbf{CH_3}$), 23.16 (-$OCH_2(CH_2)_{15}\mathbf{CH_2}CH_3$), 26.51 (-$OCH_2(CH_2)_{14}\mathbf{CH_2}CH_2CH_3$), 29.41 (-$OCH_2(CH_2)_{13}\mathbf{CH_2}(CH_2)_2CH_3$), 30.14 (-$OCH_2(CH_2)_{12}\mathbf{CH_2}(CH_2)_3CH_3$), 30.61 (-$OCH_2(CH_2)_{11}\mathbf{CH_2}(CH_2)_4CH_3$), 30.82 (-$OCH_2(CH_2)_{10}\mathbf{CH_2}(CH_2)_5CH_3$), 31.19 (-$OCH_2(CH_2)_9\mathbf{CH_2}(CH_2)_6CH_3$), 31.72 (-$OCH_2(CH_2)_8\mathbf{CH_2}(CH_2)_7CH_3$), 31.96 (-$OCH_2(CH_2)_7\mathbf{CH_2}(CH_2)_8CH_3$), 32.15 (-$OCH_2(CH_2)_6\mathbf{CH_2}(CH_2)_9CH_3$), 32.21 (-$OCH_2(CH_2)_5\mathbf{CH_2}(CH_2)_{10}CH_3$), 32.29

(-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_{11}CH_3$), 32.36 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_{12}CH_3$), 32.42 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_{13}CH_3$), 32.50 (-OCH_2CH_2**CH_2**$(CH_2)_{14}CH_3$), 32.57 (-OCH_2**CH_2**$(CH_2)_{15}CH_3$), 68.16 (-**OCH_2**$(CH_2)_{15}CH_3$), 114.45 (aromatic C–H), 126.68 (aromatic C), 129.74 (aromatic C–H), 161.66 (aromatic **C**–OCH_2), 172.18 (C=O).

*4-Icosancyloxybenzoic acid (**1s**)*. Yield = 79%. The elemental analysis (%) calc.: C 77.51, H 11.0; found: C 77.5, H 11.3. Characteristic spectroscopic data: FTIR (υ/cm^{-1}): 2960 (w, υ_{as}(C–H) of CH_3 group), 2864 (w, υ_s(C–H) of CH_3 group), 2914 (s, υ_{as}(C–H) of CH_2 group), 2850 (s, υ_s(C–H) of CH_2 group), 3064 (w, υ(C–H)aromatic), 1692 (s, υ(C=O)), 1601, 1576, and 1507 (s, m, m, υ(C=C)aromatic), 1254 (s, υ(C–O)), 1470(m, δ(C–H)). UV-Vis (λ/nm): 230 (n–σ*), 255 (π–π*), 299 (n–π*). ^{1}H NMR (δ/ppm): 0.89 (3H, t, -$OCH_2(CH_2)_{18}$**CH_3**), 1.30–1.41 (34H, m, -OCH_2CH_2**$(CH_2)_{17}$**CH_3), 1.80 (2H, m, -OCH_2**CH_2**$(CH_2)_{17}CH_3$), 4.01 (2H, t, -**OCH_2**$(CH_2)_{18}CH_3$), 6.91 (2H, d, J = 8.8 Hz, aromatic protons), 7.82 (2H, d, J = 8.8 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.02 (-$OCH_2(CH_2)_{18}$**CH_3**), 23.10 (-$OCH_2(CH_2)_{17}$**CH_2**CH_3), 26.29 (-$OCH_2(CH_2)_{16}$**CH_2**CH_2CH_3), 29.29 (-$OCH_2(CH_2)_{15}$**CH_2**$(CH_2)_2CH_3$), 30.10 (-$OCH_2(CH_2)_{14}$**CH_2**$(CH_2)_3CH_3$), 30.55 (-$OCH_2(CH_2)_{13}$**CH_2**$(CH_2)_4CH_3$), 30.77 (-$OCH_2(CH_2)_{12}$**CH_2**$(CH_2)_5CH_3$), 31.11 (-$OCH_2(CH_2)_{11}$**CH_2**$(CH_2)_6CH_3$), 31.66 (-$OCH_2(CH_2)_{10}$**CH_2**$(CH_2)_7CH_3$), 31.90 (-$OCH_2(CH_2)_9$**CH_2**$(CH_2)_8CH_3$), 32.10 (-$OCH_2(CH_2)_8$**CH_2**$(CH_2)_9CH_3$), 32.20 (-$OCH_2(CH_2)_7$**CH_2**$(CH_2)_{10}CH_3$), 32.29 (-$OCH_2(CH_2)_6$**CH_2**$(CH_2)_{11}CH_3$), 32.35 (-$OCH_2(CH_2)_5$**CH_2**$(CH_2)_{12}CH_3$), 32.41 (-$OCH_2(CH_2)_4$**CH_2**$(CH_2)_{13}CH_3$), 32.50 (-$OCH_2(CH_2)_3$**CH_2**$(CH_2)_{14}CH_3$), 32.55 (-$OCH_2(CH_2)_2$**CH_2**$(CH_2)_{15}CH_3$), 32.61 (-OCH_2CH_2**CH_2**$(CH_2)_{16}CH_3$), 32.69 (-OCH_2**CH_2**$(CH_2)_{17}CH_3$), 68.13 (-**OCH_2**$(CH_2)_{18}CH_3$), 114.41 (aromatic C–H), 126.61 (aromatic C), 129.72 (aromatic C–H), 161.61 (aromatic **C**–OCH_2), 172.11 (C=O).

*General procedure for the synthesis of bis(4-alkoxybenzoate) copper(II) complexes (**2a–s**)*

Copper(II) acetate (5 g, 25 mmol) was dissolved in 250 mL Erlenmeyer flask with 50 mL ethanol. A minimum quantity of ethanol was added to a stoichiometric amount of acid that was dissolved in another flask. The 400 mL beaker was filled with the two solutions. Sometimes a precipitate didn't form until after it had stirred overnight. The precipitate was filtered off, washed with ethanol and dried in vacuum to give the desired product.

*Bis(4-methoxybenzoate) copper(II) (**2a**)*. Yield = 77%. The elemental analysis (%) calc.: C 52.53, H 3.8, Cu 17.37; found: C 52.1, H 3.6, Cu 17.4. Molar conductivity (Λ): 9 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2938 (w, υ_{as}(C–H) of CH_3 group), 2820 (w, υ_s(C–H) of CH_3 group), 1635 (s, υ(C=O)), 1598 and 1510 (w,s, υ(C=C)aromatic), 1233 (s, υ(C–O)), 450 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 259 (π–π*+CT), 430 (n–π *), 650(d-d).

*Bis(4-ethoxybenzoate) copper(II) (**2b**)*. Yield = 77%. The elemental analysis (%) calc.: C 54.89, H 4.57, Cu 16.13; found: C 54.1, H 4.6, Cu 16.00. Molar conductivity (Λ): 8 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2930 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group., 1640 (s, υ(C=O)), 1598 and 1510 (w,s, υ(C=C)aromatic), 1253 (s, υ(C–O)), 450 (m, υ(Cu–O)). UV–Vis (λ/nm): 250 (n–σ*), 259 (π–π*+ CT), 437 (n–π *), 656 (d-d).

*Bis(4-proploxybenzoate) copper(II) (**2c**)*. Yield = 70%. The elemental analysis (%) calc.: C 56.93, H 5.21, Cu 15.6; found: C 56.23, H 4.98, Cu 14.97. Molar conductivity (Λ): 10 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2932 (w-m, υ_{as}(C–H) of CH_2 group), 2827 (w-m, υ_s(C–H) of CH_2 group), 1642 (s, υ(C=O)), 1598 and 1510 (w, s, υ(C=C)aromatic), 1243 (s, υ(C–O)), 450 (m, υ(Cu–O)). UV–Vis

(λ/nm): 230 (n–σ*), 259 (π–π*+CT), 433 (n–π *), 650 (d-d).

Bis(4-butyloxybenzoate) copper(II) ***(2d)***. Yield = 75%. The elemental analysis (%) calc.: C 59.5, H 5.78, Cu 14.1; found: C 59.7, H 5.6, Cu 14.4. Molar conductivity (Λ): 11 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 1640 (s, υ(C=O)), 1598 and 1510 (w, s, υ(C=C)aromatic), 1233 (s, υ(C–O)), 450 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 257 (π–π*+CT), 430 (n–π*), 650 (d-d).

Bis(4-pentyloxylbenzoate) copper(II) ***(2e)***. Yield = 85%. The elemental analysis (%) calc.: C 60.31, H 6.28, Cu 13.29; found: C 59.30, H 6.6, Cu 13.4. Molar conductivity (Λ): 8 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2932 (w-m, υ_{as}(C–H) of CH_2 group), 2825 (w-m, υ_s(C–H) of CH_2 group), 1635 (s, υ(C=O)), 1598 and 1510 (w, s, υ(C=C)aromatic), 1223 (s, υ(C–O)), 450 (m, υ(Cu–O)). UV–Vis (λ/nm): 230 (n–σ*), 259 (π–π*+CT), 420 (n–π *), 640 (d-d).

Bis(4-hexyloxylbenzoate) copper(II) ***(2f)***. Yield = 80%. The elemental analysis (%) calc.: C 61.7, H 6.72, Cu 12.56; found: C 61.1, H 6.6, Cu 12.4. Molar conductivity (Λ): 9 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 1630 (s, υ(C=O)), 1596 and 1510 (w, s, υ(C=C)aromatic), 1233 (s, υ(C–O)), 452 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 255 (π–π*+CT), 430 (n–π*), 650 (d-d).

Bis(4-heptyloxylbenzoate) copper(II) ***(2g)***. Yield = 85%. The elemental analysis (%) calc.: C 62.29, H 7.12, Cu 11.9; found: C 62.1, H 7.6, Cu 11.4. Molar conductivity (Λ): 9 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2958 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2930 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 1640 (s, υ(C=O)), 1597 and 1511 (w, s, υ(C=C) aromatic), 1233 (s, υ(C–O)), 455 (m, υ(Cu–O)). UV–Vis (λ/nm): 230 (n–σ*), 257 (π–π*+CT), 420 (n–π *), 655 (d-d).

Bis(4-octyloxylbenzoate) copper(II) ***(2h)***. Yield = 76%. The elemental analysis (%) calc.: C 64.11, H 7.47, Cu 11.3; found: C 64.1, H 7.6, Cu 11.4. Molar conductivity (Λ): 11 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2830 (w-m, υ_s(C–H) of CH_2 group), 1630 (s, υ(C=O)), 1596 and 1511 (w, s, υ(C=C)aromatic), 1222 (s, υ(C–O)), 455 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 259 (π–π*+CT), 433 (n–π*), 650 (d-d).

Bis(4-nonyloxylbenzoate) copper(II) ***(2i)***. Yield = 80%. The elemental analysis (%) calc.: C 65.13, H 7.8, Cu 10.7; found: C 64.98, H 7.6, Cu 10.4. Molar conductivity (Λ): 8 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2946 (w, υ_{as}(C–H) of CH_3 group), 2825 (w, υ_s(C–H) of CH_3 group), 2932 (w-m, υ_{as}(C–H) of CH_2 group), 2827 (w-m, υ_s(C–H) of CH_2 group), 1643 (s, υ(C=O)), 1598 and 1515 (w, s, υ(C=C)aromatic), 1234 (s, υ(C–O)), 454 (m, υ(Cu–O)). UV–Vis (λ/nm): 230 (n–σ*), 257 (π–π*+CT), 420 (n–π*), 640 (d-d).

Bis(4-decyloxylbenzoate) copper(II) ***(2j)***. Yield = 70%. The elemental analysis (%) calc.: C 66.07, H 8.09, Cu 10.28; found: C 66.1, H 10.6, Cu 10.3. Molar conductivity (Λ): 10 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2940 (w, υ_{as}(C–H) of CH_3 group), 2825 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 1640 (s, υ(C=O)), 1597 and 1512 (w,s, υ(C=C)aromatic), 1223 (s, υ(C–O)), 455 (m, υ(Cu–O)). UV–Vis (λ/nm): 256 (n–σ*), 259 (π–π*+CT), 433 (n–π*), 645 (d-d).

Bis(4-undecyloxylbenzoate) copper(II) ***(2k)***. Yield = 70%. The elemental analysis (%) calc.: C 66.9, H 8.36, Cu 9.83; found: C 66.0, H 8.6, Cu 10.4.Molar conductivity (Λ): 9 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2946 (w, υ_{as}(C–H) of CH_3 group), 2820 (w, υ_s(C–H) of CH_3 group), 2930 (w-m, υ_{as}(C–H) of CH_2 group), 2826 (w-m, υ_s(C–H) of CH_2 group), 1630 (s, *υ*(C=O)), 1598 and 1510 (w, s, υ(C=C)aromatic), 1233 (s, υ(C–O)), 452 (m, υ(Cu–O)). UV–Vis (λ/nm): 237 (n–σ*), 259 (π–π*+CT), 435 (n–π*), 640 (d-d).

Bis(4-dodecyloxylbenzoate) copper(II) ***(2l)***. Yield = 74%. The elemental analysis (%) calc.: C 67.7, H 8.83, Cu 9.05; found: C 67.0, H 8.6, Cu 8.94. Molar conductivity (Λ): 8 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3058 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2820 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2827 (w-m, υ_s(C–H) of CH_2 group), 1627 (s, *υ*(C=O)), 1596 and 1513 (w, s, υ(C=C)aromatic), 1223 (s, υ(C–O)), 457 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 254 (π–π*+CT), 420 (n–π*), 660(d-d).

Bis(4-tridecyloxylbenzoate) copper(II) ***(2m)***. Yield = 80%. The elemental analysis (%) calc.: C 68.42, H 8.83, Cu 9.05; found: C 68.1, H 8.06, Cu 9.00. Molar conductivity (Λ): 8 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2947 (w, υ_{as}(C–H) of CH_3 group), 2824 (w, υ_s(C–H) of CH_3 group), 2930 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 1630 (s, *υ*(C=O)), 1596 and 1515 (w, s, υ(C=C)aromatic), 1223 (s, υ(C–O)), 457 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 259 (π–π*+CT), 433 (n–π*), 620 (d-d).

Bis(4-tetrdecyloxylbenzoate) copper(II) ***(2n)***. Yield = 70%. The elemental analysis (%) calc.: C 69.08, H 9.04, Cu 8.70; found: C 69.1, H 9.6, Cu 9.04. Molar conductivity (Λ): 9 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2946 (w, υ_{as}(C–H) of CH_3 group), 2825 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2827 (w-m, υ_s(C–H) of CH_2 group), 1633 (s, *υ*(C=O)), 1594 and 1509 (w, s, υ(C=C)aromatic), 1233 (s, υ(C–O)), 450 (m, υ(Cu–O)). UV–Vis (λ/nm): 254 (n–σ*), 257 (π–π*+CT), 420 (n–π*), 650 (d-d).

Bis(4-pentdecyloxylbenzoate) copper(II) ***(2o)***. Yield = 75%. The elemental analysis (%) calc.: C 69.70, H 9.24, Cu 8.38; found: C 68.81, H 8.98, Cu 8.4. Molar conductivity (Λ): 10 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H) aromatic), 2945 (w, υ_{as}(C–H) of CH_3 group), 2822 (w, υ_s(C–H) of CH_3 group), 2933 (w-m, υ_{as}(C–H) of CH_2 group), 2826 (w-m, υ_s(C–H) of CH_2 group), 1635 (s, *υ*(C=O)), 1596 and 1510 (w, s, υ(C=C) aromatic), 1223 (s, υ(C–O)), 455 (m, υ(Cu–O)). UV–Vis (λ/nm): 230 (n–σ*), 259 (π–π*+CT), 425 (n–π*), 630 (d-d).

Bis(4-hexadecyloxylbenzoate) copper(II) ***(2p)***. Yield = 80%. The elemental analysis (%) calc.: C 70.27, H 9.42, Cu 8.38; found: C 70.4, H 10.06, Cu 9.04. Molar conductivity (Λ): 8 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2944 (w, υ_{as}(C–H) of CH_3 group), 2824 (w, υ_s(C–H) of CH_3 group), 2930 (w-m, υ_{as}(C–H) of CH_2 group), 2829 (w-m, υ_s(C–H) of CH_2 group), 1627 (s, *υ*(C=O)), 1598 and 1513 (w, s, υ(C=C)aromatic), 1253 (s, υ(C–O)), 457 (m, υ(Cu–O)). UV–Vis (λ/nm): 234 (n–σ*), 257 (π–π*+CT), 450 (n–π*), 655 (d-d).

Bis(4-heptadecyloxylbenzoate) copper(II) ***(2q)***. Yield = 65%. The elemental analysis (%) calc.: C 70.80, H 9.58, Cu 7.80; found: C 71.1, H 9.60, Cu 8.20. Molar conductivity (Λ): 11 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2823 (w, υ_s(C–H) of CH_3 group), 2932 (w-m, υ_{as}(C–H) of CH_2 group), 2826 (w-m, υ_s(C–H) of CH_2 group), 1627 (s, *υ*(C=O)), 1598 and 1510 (w, s, υ(C=C)aromatic), 1233 (s, υ(C–O)), 456 (m, υ(Cu–O)). UV–Vis (λ/nm): 230 (n–σ*), 257 (π–π*+CT), 430 (n–π*), 650 (d-d).

Bis(4-octadecyloxylbenzoate) copper(II) ***(2r)***. Yield = 70%. The elemental analysis (%) calc.: C 71.30, H 9.74, Cu 7.54; found: C 70.98, H 10.03, Cu 8.03. Molar conductivity (Λ): 10 $S.cm^2.mol^{-}$

^{1}. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H)aromatic), 2946 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 2934 (w-m, υ_{as}(C–H) of CH_2 group), 2830 (w-m, υ_s(C–H) of CH_2 group), 1630 (s, *υ*(C=O)), 1597 and 1510 (w,s, υ(C=C)aromatic), 1223 (s, υ(C–O)), 452 (m, υ(Cu–O)). UV–Vis (λ/nm): 244 (n–σ*), 259 (π–π*+CT), 433 (n–π*), 640 (d-d).

*Bis(4-icosancyloxylbenzoate) copper(II) (**2s**)*. Yield = 73%. The elemental analysis (%) calc.: C 72.20, H 10.02, Cu 7.07; found: C 72.1, H 9.73, Cu 7.4. Molar conductivity (Λ): 9 S.cm^2.mol^{-1}. FTIR (υ/cm^{-1}): 3058 (w, υ(C–H)aromatic), 2949 (w, υ_{as}(C–H) of CH_3 group), 2828 (w, υ_s(C–H) of CH_3 group), 2935 (w-m, υ_{as}(C–H) of CH_2 group), 2826 (w-m, υ_s(C–H) of CH_2 group), 1627 (s, *υ*(C=O)), 1595 and 1513 (w, s, υ(C=C)aromatic), 1230 (s, υ(C–O)), 449 (m, υ(Cu–O)). UV–Vis (λ/nm): 254 (n–σ*), 257 (π–π*+CT), 435 (n–π*), 655 (d-d).

RESULTS AND DISCUSSION

Synthesis and characterization of compounds

A full series of 4-alkoxybenzoic acid (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20) ***(1a–s)*** was prepared starting from 4-hydroxybenzoate as a new, efficient, and practical synthetic procedure (Scheme 1). Research through the literature revealed that no synthetic procedure could help in synthesizing a full series of 4-alkoxybenzoic acid compounds. All of the synthetic procedures reported so far prepare 4-alkoxybenzoic acid compounds (alkoxy: (OC_nH_{2n+1}), n = 1–12) through the reaction of 4-hydroxybenzoic acid and appropriate alkyl bromide in strong basic conditions. In this work, we treated 4-alkoxybenzoate with KOH in a mixture of (H_2O:EtOH) (1:1) to produce the corresponding potassium-4-alkoxybenzoates, then, convert these compounds to the corresponding 4-alkoxybenzoic acid derivatives with HCl. Interestingly, this synthetic procedure can be applied for full series of alkyl chain (n) from 1 to 20.

A series of bis(4-alkoxybenzoate) copper(II) complexes (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20) ***(2a–s)*** was prepared by the stirring of a corresponding 4-alkoxybenzoic acid compound with copper(II) acetate in ethanol, and under inert and ambient conditions. Scheme 1 shows the synthetic diagram of the prepared compound.

The mesogens (***1a–s***) and their copper(II) complexes (***2a–s***) were identified using a variety of methods, including molar conductivity measurements, atomic absorption (for copper(II) complexes), FTIR, UV–Vis, ^{1}H NMR, ^{13}C NMR, and microelemental analysis. The experimental section provides an illustration of these data.

The data obtained from the C, H, and N microelemental examinations demonstrate a strong agreement between the suggested and real formulas. The FTIR spectra of ***1a–s*** often show certain characteristic bands that are associated with the C–H, C=C, and C=O functional groups [27]. The bands associated with the C–H and C=C functional groups found in the spectra of the respective ligands were nearly identical in the FTIR spectra of the copper(II) complexes (***2a–s***), but with minor variations in their locations or appearance. Furthermore, the spectra of the corresponding Cu(II) complexes (***2a–s***) showed a considerable change in frequency of the band resulting from the stretching vibration of the C=O group that was observed in the spectra of carboxylic acid compounds (***1a–s***). This provides proof that the O atom of the C=O group is involved in the binding process between an organic ligand (carboxylic acid molecule) and the copper (II) ion. Coordination to a metal ion causes a C=O carboxylic acid group's stretching vibration to shift to lower frequencies, as has already been observed and documented [31-32]. In the ^{1}H NMR and ^{13}C NMR spectra of carboxylic acid molecules, several signals corresponding to different carbon and proton nuclei are detected (for example, refer to Figure 1). The experimental section shows the specifics of these signals and how they are assigned to each created chemical.

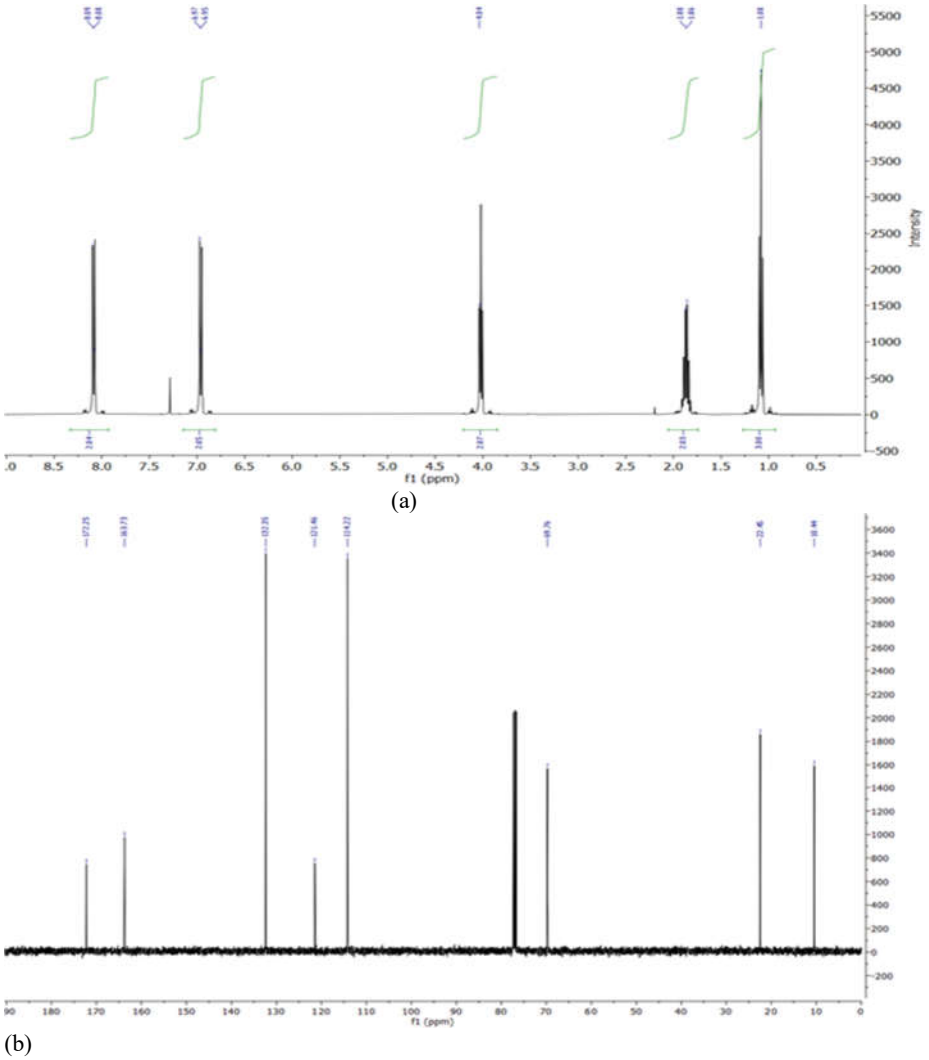


Figure 1. NMR spectra of *1c* (a) ^{1}H NMR and b) ^{13}C NMR.

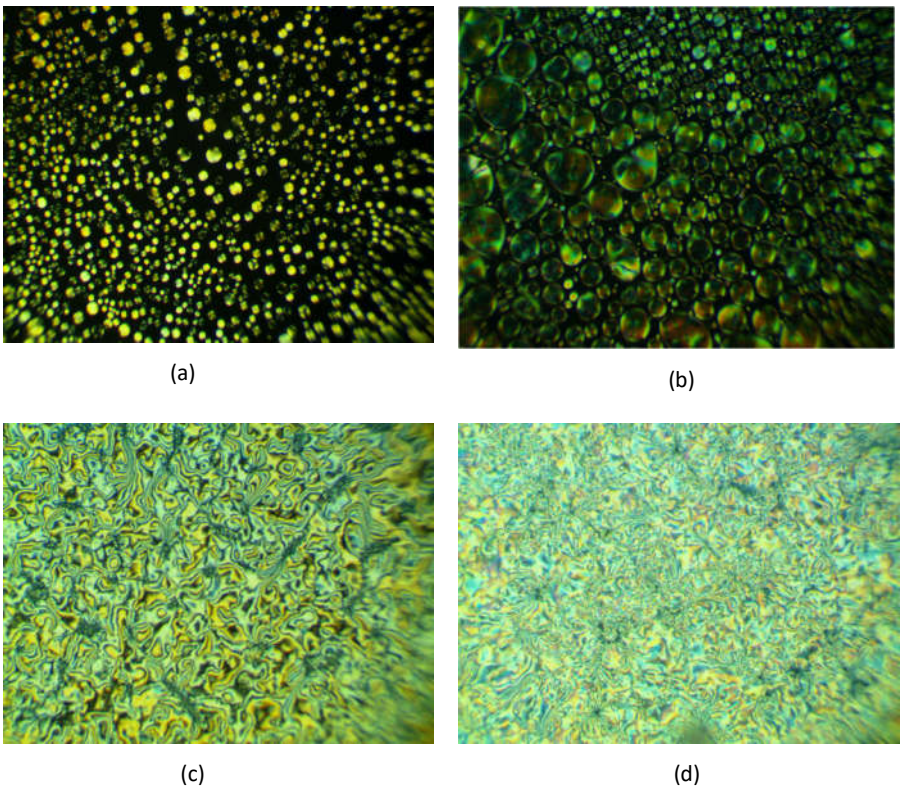
UV–Vis spectra of 4-alkoxybenzoic acid compounds ***(1a–s)*** displayed three absorption peaks at the ranges: (223–234 nm), (255–310 nm), and (270–326 nm). These peaks are attributed to the n–σ*, π–π*, and n–π* transitions respectively. Upon coordination of the prepared 4-alkoxybenzoic acid compounds to Cu(II) ion, these transitions were discovered to be moved to wave numbers that were either higher or lower. Furthermore, the strong π–π* band and the band resulting from the charge transfer (CT) transition were either merged or slightly separated in all complexes. Furthermore, the spectra of all complexes exhibited a broad band which mainly due to d-d transitions [33]. The experimental section includes a list of the UV-Vis spectral data information.

The molar conductivity values of copper(II) complexes ***(2a–s)*** in acetone ($1x10^{-3}$M), are in the range (8–11) S. cm^2. mol^{-1}, confirming their nonelectrolytic nature [34].

The data provided by FTIR, UV–Vis, conductivity measurements, and microelemental analysis, revealed the bidentate behaviour of 4-alkoxybenzoic acid compounds toward copper(II) ions. Two molecules of 4-alkoxybenzoic acid are binding to the Cu atom through two O atoms, produced a 4-coordinate mononuclear complex having the standard formula $[Cu^{II}(L)_2]$ (where L: 4-alkoxybenzoic acid (alkoxy: ($OCnH_2n_{+1}$), n = 1–18, 20) derivative).

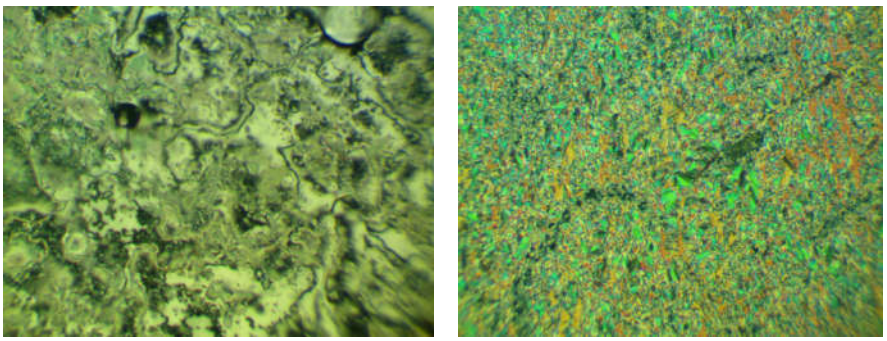
Liquid-crystalline behavior of the prepared compounds

The liquid crystalline behavior of the synthesized compounds was assessed by the use of polarized light optical microscope (POM) technology. Overall, the study revealed that every component of 4-alkoxybenzoic acid (alkoxy: (OC_nH_{2n+1}), n = 3–18, 20) ***(1a–s)*** are materials that are mesomorphic and exhibit enantiotropic liquid crystal properties. (***1a***, ***1b***, and ***1s*** show no liquid crystal properties). Furthermore, the mesomorphic properties of these compounds are fully disappeared upon coordination with copper(II) ion. Therefore, bis(4-alkoxybenzoate) copper(II) complexes (alkoxy: (OC_nH_{2n+1}), n=1–18, 20) ***(2a–s)*** displays no mesomorphic characteristics; it melts to an isotropic liquid. Table 1 shows the specifics of the mesophase transitions, and Figure 2 shows instances of optical micrographs of these compounds.



(a) (b)

(c) (d)



(e) (f)

Figure 2. Optical micrographs (magnification:×300) of (a) the nematic droplet-like texture obtained for ***1c*** at 143 °C upon cooling; (b) the nematic droplet-like texture obtained for ***1h*** at 130 °C upon cooling; (c) the schlieren nematic texture detected for ***1l*** at 138 °C upon cooling; (d) the schlieren nematic texture detected for ***1n*** at 141 °C upon heating; (e) the nematic thread-like texture observed for ***1d*** at 159 °C upon cooling; (f) the fan-shape texture observed for ***1j*** at 121 °C upon heating.

Table 1 makes it evident that compounds ***1c–f*** only showed nematic mesophase when heated and cooled, as expected based on their characteristic thread- or droplet-like textures. Upon heating and chilling, the remaining compounds, ***1g*** to ***1r***, displayed both smectic and nematic mesophases. While nematic mesophase was determined by the characteristic thread-like or droplet-like texture, smectic mesophase was characterized by the SmA or SmC. These outcomes closely resemble those that were previously attained. [33].

Upon complexation of 4-alkoxybenzoic acid derivatives with coppe(II), the liquid crystal behaviour and properties are fully disappeared. This discrepancy can result from the two series of chemicals' dissimilar stereochemical structures.

In general, a mesogen's clearance temperature may vary depending on the length of the hydrocarbon chain. Accordingly, the van der Waals interactions in a compound grow with chain length, raising the clearing point. However, the hydrocarbon chain's flexibility may interfere with the lateral core-core interactions, which lowers a compound's clearing point. The clearing temperatures of 4-alkoxybenzoic acid (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20) ***(1a–s)*** are shown to decrease as the chain length increases, as displayed in Figure 3 (this figure clearly illustrates the odd-even effect in both series). This suggests that the random mobility of hydrocarbon chains appears to govern the melting process, with the van der Waals interactions between chains having less of an impact. [8, 34, 35].

Table 1. Phase transitions and their temperatures for the prepared compounds obtained by POM.

Compound	n	Phase transitions (T / °C) first heating	Phase transitions (T / °C) first cooling
1$_a$	1	Cr-I (201.0)	-
1$_b$	2	Cr-I (213.0)	-
1$_c$	3	Cr-N (150.0) N-I (165.0)	I-N (146.0) N-Cr (141.0)
1$_d$	4	Cr-N (170.0) N-I (174.0)	I-N (171.0) N-Cr (153.0)
1$_e$	5	Cr-N (157.0) N-I (160.0)	I-N (155.0) N-Cr (123.0)
1$_f$	6	Cr-N (161.0) N-I (167.0)	I-N (163.0) N-Cr (112.0)
1$_g$	7	Cr-SmC (100.0) SmC-N (150.0) N-I (154.0)	I-N (147.0) N-SmC (106.0) SmC-Cr (92.0)
1$_h$	8	Cr-SmA (112.0) SmA-N (155.0) N-I (158.0)	I-N (153.0) N-SmA (110.0) SmA-Cr (101.0)
1$_i$	9	Cr-SmA (106.0) SmA-N (147.0) N-I (150.0)	I-N (149.0) N-SmA (128.0) SmA-Cr (94.0)
1$_j$	10	Cr-SmA (109.0) SmA-N (152.0) N-I (155.0)	I-N (151.0) N-SmA (130.0) SmA-Cr (99.0)
1$_k$	11	Cr-SmA (102.0) SmA-N (141.0) N-I (145.0)	I-N (143.0) N-SmA (125.0) SmA-Cr (91.0)
1$_l$	12	Cr-SmA (97.0) SmA-N (145.0) N-I (149.0)	I-N (141.0) N-SmA (133.0) SmA-Cr (92.0)
1$_m$	13	Cr-SmA (95.0) SmA-N (135.0) N-I (140.0)	I-N (138.0) N-SmA (128.0) SmA-Cr (90.0)
1$_n$	14	Cr-SmA (90.0) SmA-N (139.0) N-I (144.0)	I-N (142.0) N-SmA (136.0) SmA-Cr (94.0)
1o	15	Cr-SmA (86.0) SmA-N (129.0) N-I (130.0)	I-N (128.0) N-SmA (121.0) SmA-Cr (85.0)
1$_p$	16	Cr-SmA (105.0) SmA-I (132.0) Cr-I (135.0)	I-N (133.0) N-SmA (127.0) SmA-Cr (92.0)
1$_q$	17	Cr-SmA (100.0) SmA-I (123.0) Cr-I (127.0)	I-N (124.0) N-SmA (117.0) SmA-Cr (90.0)
1r	18	Cr-SmA (110.0) SmA-I (127.0) Cr-I (130.0)	I-N (128.0) N-SmA (115.0) SmA-Cr (94.0)
1s	20	Cr-I (100.0)	-

Cr: Crystalline solid, SmA: Smectic A mesophase, SmC: Smectic C mesophase, N: Nematic mesophase, I: Isotropic liquid, n: alkyl chain length.

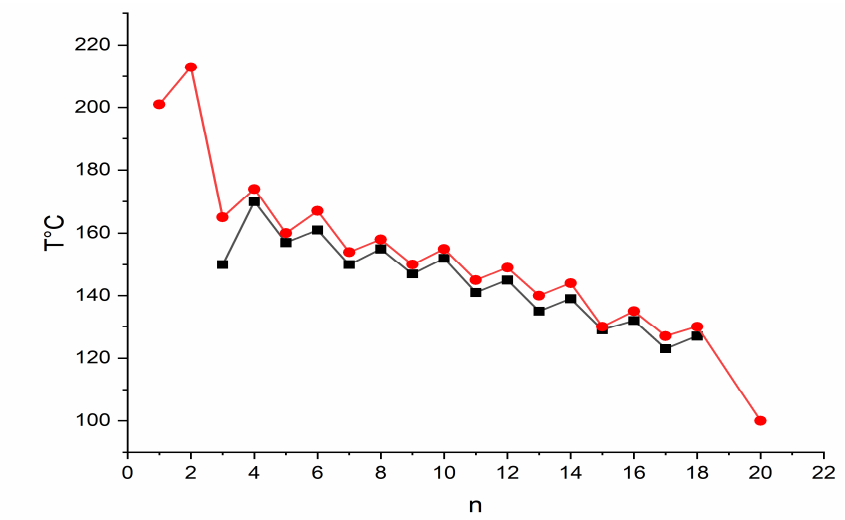


Figure 3. Clearing temperature (T_c) (red line) and temperature of nematic mesophase (black line) as a function of alkyl chain length for 4-alkoxybenzoic acid series.

CONCLUSIONS

Treating 4-alkoxybenzoate with KOH in a mixture of (H_2O:EtOH) (1:1) and neutralizing with HCl produced a full series of 4-alkoxybenzoic acid derivatives (alkoxy: (OC_nH_{2n+1}), n = 1–18, 20) ***(1a–s)***. This can be considered as a new, efficient, and practical synthetic procedure. All of these compounds are mesomorphic materials displaying enantiotropic liquid crystal properties (***1a***, ***1b***, and ***1s*** show no liquid crystal properties). Compounds ***1c–f*** displayed only nematic mesophase when heated and cooled; this was explained by the texture's characteristic thread- or droplet-like appearance. While the rest compounds ***1g*** to ***1r*** showed both of smectic and nematic mesophases upon heating and cooling. Upon complexation of 4-alkoxybenzoic acid derivatives with coppe(II), the liquid crystal behaviour and properties are fully disappeared. This difference may be due to the different streochemical structure of the two series of compounds.

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