Synthesis and Self-assembly of Novel Nanofeather-like Fluorescent Alkyloxy-Containing Diphenyl Ether Organogelators

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ABSTRACT: In this study, novel fluorescent low molecular-weight organogelators are derived from diphenyl ethers and substituted with para-alkoxy groups of different aliphatic chain lengths. The present research promotes the preparation of innovative nanofeather-like assemblies from the synthesized diphenyl ether-derived organogelators. The gelation performance of the prepared alkoxy-substituted diphenyl ethers was reported. The synthesis procedure was achieved by using a base-catalyzed reaction of hydroxyl-substituted diphenyl with various alcohols of different aliphatic chain lengths. The chemical structures of the synthesized diphenyl ether derivatives were studied by $^1$H/$^13$C NMR and infrared spectroscopy. Fluorescence and UV–vis absorption spectral analyses showed solvatochromism. The diphenyl ether derivatives with longer alkoxy terminal substituents showed enhanced thermoreversible gelation activity as compared to the diphenyl ether derivatives with shorter alkoxy terminal substituents. The morphological properties of the self-assembled diphenyl ethers were studied by transmission electron microscopy and scanning electron microscopy, which showed supramolecular architectures of highly ordered nanofeathers, enforced by van der Waals interactions and $\pi$-stacks. Depending on the length of the aliphatic tail, different morphologies were detected, including nanofeathers, nanofibers, and nanosheets. The antimicrobial and cytotoxic properties of the prepared diphenyl ether-derived organogelators were examined to confirm their possible use in various fields like drug delivery systems.

1. INTRODUCTION

Low molecular-weight organogelators are becoming more relevant owing to their thermal reversibility, sensitivity to chemicals, and diversity of macroscaled architectures. Biomedical, foodstuff, and cosmetic applications have all exploited organogel technology. The self-assembly of small organogelator molecules occurs by the entrapment of tolerable volumes of solvents, providing beneficial characteristics for various applications. Self-assembled structures can introduce optoelectronic characteristics like enhancing emission and charge transfer. A supramolecular organogel can be described as a soft matter consisting of a viscoelastic non-flowing fluid due to the existence of an organogelator capable of self-assembling into three-dimensional supramolecular architectures. Those supramolecular architectures can be generated in a variety of morphologies, such as nanofeathers, nanoribbons, nanosheets, nanorods, and nanoﬁbers. Self-assembly of organogelators has interesting research in many fields, such as catalysis, sensors, pollutant removal, drug self-delivery, and tissue engineering. The self-assembly processes are usually driven by various types of attraction forces such as physical bonding, chemical bond formation, phase transition, and/or cross-linking. Recently, the distinctive capability of organic gelators to uphold solvents by non-covalent bond formation, like H-bonds, $\pi$-stacks, and van der Waals forces, has received considerable attention. The organogelator molecular entities typically self-assemble into highly ordered macro-molecular architectures without exchanging into their dense structural form. Low molecular-weight organogels have been used in the formation of nanoporous substrates, removal of pollutants, enhancement of rheological properties in cosmetic products, drug delivery, sensors, engineering of tissues, foodstuffs, and polymer crystalline nucleation substances.

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the development of luminous organogelators based on alkoxy-substituted diphenyl ethers has been described in limited studies.\textsuperscript{34,35} Moreover, the development of fluorescent nanofeather-like organic gelators based on alkoxy-substituted diphenyl ethers has not been reported yet. In the current study, organogelators with novel fluorescent alkoxy-substituted diphenyl ethers have been synthesized, characterized, and self-assembled for potential optoelectronic applications. Organo-gels made of diphenyl ether hard cores and flexible terminal alkoxy chains have been described. The synthesis procedure was achieved by a base-catalyzed reaction of hydroxyl-substituted diphenyl with various alcohols of different aliphatic chain lengths. As a result, diphenyl ethers with high emission and extended conjugation were produced. The emission of these alkoxy-substituted diphenyl ethers with various alkoxy chain lengths was reported. As a consequence, they could be considered proper materials for optoelectronic display devices with reduced energy usage, in particular, portable displays.\textsuperscript{36,37} Alkoxy-substituted diphenyl ether derivatives were tested for gelation and supramolecular characteristics in different solvents. The critical gel concentration (CGC) of a formed gel was recorded in various solvents. Alkoxy-substituted diphenyl ethers were tested for antibacterial efficacy and cytotoxicity. Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized to examine the nanostructured morphologies of self-assembled fluorescent organogels. The prepared diphenyl ethers displayed solvatochromic and solvatofluorochromic properties.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. The materials utilized in the current research were sourced from commercial sources. n-Iodoalkane, 4-(4-iodophenyl)phenol, potash, and N,N-dimethylmethanamide were purchased from Merck and Sigma-Aldrich (Egypt). All solvents were of spectroscopic grade and obtained from Fluka and Sigma-Aldrich (Egypt). The organogelators were synthesized according to previous procedures.\textsuperscript{38} Under ultraviolet light, aluminum plates coated with a thin layer of silica gel (60) were used to monitor the reaction progress by thin layer chromatography (TLC) (UV layer of silica gel (60) were used to monitor the reaction. Under ultraviolet light, aluminum plates coated with a thin layer of silica gel (60) were used to monitor the reaction progress by thin layer chromatography (TLC) (UV layer of silica gel (60) were used to monitor the reaction progress by thin layer chromatography (TLC) (UV).

2.2. Synthesis Procedures. 2.2.1. General Synthesis of 4-Alkoxy-4′-iodobiphenyl. n-Iodoalkane, 4-(4-iodophenyl)phenol, and potash were dissolved in N,N-dimethylmethanamide in a nitrogen atmosphere. The provided solution was stirred for 9 h till TLC indicated a complete consumption of 4-(4-iodophenyl)phenol. The reaction mixture was then poured into crushed ice. The generated precipitate was filtered, washed with distilled water, and air-dried.

2.2.2. 4-Propoxyloxy-4′-iodobiphenyl 1. 4-Propoxyloxy-4-iodobiphenyl 1 was synthesized from an admixture of 4-(4-iodophenyl)phenol (1.52 g; 5 mmol), n-iodopropane (1.72 g, 8.5 mmol), dimethylformamide (DMF) (10 mL), and potash (1.40 g; 10 mmol) and re-crystallized from absolute ethanol to give a white powder (1.71 g; 91%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.78 (d, 2H), 7.51 (d, 2H), 7.32 (d, 2H), 7.00 (d, 2H), 4.03 (t, 2H) 1.85 (m, 2H), 1.52 (m, 2H), 1.41 (m, 4H), 0.97 (t, 3H); IR (\textit{\nu/cm}^{-1}): 2953, 2861; Elemental Analysis (C\textsubscript{25}H\textsubscript{21}IO): 380.26 Calcd: C, 56.85; H, 5.57; Found: C, 56.77; H, 5.42.

2.2.3. 4-Hexyloxy-4′-iodobiphenyl 2. It was synthesized from a mixture of 4-(4-iodophenyl)phenol (1.73 g; 5 mmol), n-iodoheaxane (1.75 g; 8.5 mmol), DMF (10 mL), and potash (1.40 g; 10 mmol) and re-crystallized from absolute ethanol to give a white powder (1.71 g; 91%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.78 (d, 2H), 7.51 (d, 2H), 7.32 (d, 2H), 7.00 (d, 2H), 4.03 (t, 2H) 1.85 (m, 2H), 1.52 (m, 2H), 1.41 (m, 4H), 0.97 (t, 3H); IR (\textit{\nu/cm}^{-1}): 2953, 2861; Elemental Analysis (C\textsubscript{25}H\textsubscript{21}IO): 380.26 Calcd: C, 56.85; H, 5.57; Found: C, 56.77; H, 5.42.

2.2.4. 4-Undecyloxy-4′-iodobiphenyl 3. It was synthesized from an admixture of 4-(4-iodophenyl)phenol (1.98 g; 5 mmol), n-iodoundecane (1.75 g; 6 mmol), DMF (10 mL), and potash (1.40 g; 10 mmol) and re-crystallized from absolute ethanol to give a white powder (2.21 g; 95%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.76 (d, 2H), 7.50 (d, 2H), 7.34 (d, 2H), 6.98 (d, 2H), 4.03 (t, 2H), 1.83 (m, 2H), 1.49 (m, 2H), 1.37 (m, 16H), 0.92 (t, 3H); \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}); IR (\textit{\nu/cm}^{-1}): 2916, 2847; Elemental Analysis (C\textsubscript{29}H\textsubscript{25}IO): 464.42 Calcd: C, 62.07; H, 7.16. Found: C, 61.92; H, 7.08.

2.3. Gelation Study. According to previous procedures,\textsuperscript{39} the synthesized organogelators 3a–c were dissolved in various solvents and boiled in a sealed glass tube to produce a colorless medium and then cooled back to room temperature to generate the corresponding organogels. The organogels were formed in 15–25 min. The gelation time usually depends on the gelator’s total content and the aliphatic tail length. The gelation process was verified by the “stable-to-inversion” technique as designated by the solvent disappearance. The reversibility was inspected by increasing the temperature (2°C/min) of the organogel-containing tube and recording the gel melting point at which the organogel falls down. The above procedure was carried out several times to indicate good reversibility.

2.4. Apparatus and Methods. 2.4.1. Spectroscopic Characterization. The melting points were recorded by differential scanning calorimetry (TA2920). Bruker Avance 400 MHz was used to collect the \textsuperscript{1}H/\textsuperscript{13}C NMR spectra. For the elemental analysis, PerkinElmer 2400 (United States) was employed. UV–vis absorption spectra were measured using an Ultraviolet Agilent system from the Cary Series. Varian Cary Eclipse was utilized to study fluorescence and quantum yields (QY). To measure fluorescence QY, both rhodamine 101 (QY = 0.96) and rhodamine 6G (QY = 0.95) were used in ethyl alcohol (100%) as standards. The infrared spectra were obtained by Fourier transform infrared (FT-IR) using Bruker Vector 33.

2.4.2. Morphological Characterization. The morphology of 3a (partial gel) was studied by JEOL 1230 TEM (Japan). The partial organogel of 3a in n-octanol was diluted and dropped onto a copper grid for TEM analysis. The SEM studies of 3b and 3c were carried out using the Quanta FEG 250 instrument (Republic of Czech). n-Octanol was used to prepare organogels from the corresponding gelators, which were subsequently air-dried on a piece of glass. The Au-coated dried gel was annealed at 45°C overnight. The diameters of the produced supramolecular structures were measured using the ImageJ program (SEM).

2.5. Cytotoxic (In Vitro) and Antimicrobial Studies. The skin fibroblast cell line (BJ1) was utilized to carry out the cytotoxic study according to the MTT proliferation proce-

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3. RESULTS AND DISCUSSION

3.1. Synthesis and Chemistry. The main aim of the current study is to synthesize novel fluorescent diphenyl ether gelators substituted with para-alkoxy groups of different aliphatic chain lengths. The synthesis was performed by reacting hydroxyl-substituted diphenyl with various alcohols of different aliphatic chain lengths. As shown in Scheme 1, the alkoxy-substituted diphenyl ethers (3a, 3b, and 3c) were prepared in comparatively high yields by treating a mixture of 4-alkoxy-4′-iodobiphenyl and n-alkanol with K$_2$CO$_3$ in DMF at room temperature. $^1$H/$^{13}$C NMR and infrared analyses were utilized to verify the chemical structure of the synthesized diphenyl ethers 3a–c. The $^1$H NMR spectral analysis of 3a–c showed distinctive peaks for the alkyl groups ranging from ~0.92 to ~4.03 ppm. The FT-IR spectral analysis of 3a–c displayed strong absorption bands of alkyl substituents at ~2950 and ~2860 cm$^{-1}$.

3.2. Photophysical Studies. A light-responsive compound is able to transform its physical and/or chemical properties in response to a light stimulus. In the current study, some selected solvents were utilized to inspect both absorption and emission behaviors of the prepared diphenyl ethers, as demonstrated in Table 1. Both emission and absorption maxima were determined in a range of solvents like dimethyl sulfoxide (DMSO), acetonitrile, hexane, n-octanol, tetrahydrofuran (THF), absolute ethanol, DMF, toluene, benzene, CH$_2$Cl$_2$, and n-propanol. Figure 1 displays the solution of 3b in DMSO under visible and ultraviolet lights. It was observed that all diphenyl ethers absorb light in the ultraviolet–visible spectrum range. It can be concluded that the π→π* transition is the main reason for these absorption peaks. The absorption maxima were observed to increase when extending the aliphatic tail length, indicating that the excitation state of the shorter aliphatic tail-bearing diphenyl ether is less than that of the longer aliphatic chain-bearing diphenyl ether. When the aliphatic tail length was increased, the absorption wavelength was found to increase in association with a decrease in the emission wavelength. Solvatochromic behavior was detected in the absorption and emission spectra as a function of solvent polarity. Both absorption and fluorescence wavelengths were found to increase when increasing the solvent polarity, indicating positive solvatochromism. Moreover, the quantum yields were observed to decrease when the aliphatic tail length increased.

3.3. Gelation Studies. The self-assembled nanofeather-like structures of the alkoxy-substituted π-conjugated diphenyl ethers have been reported. Light emission of a material has been a key character when being responsive to the surrounding environment. For instance, the generation of fluorescent supramolecular architectures could result in considerable modulated impact on the emission intensity and/or wavelength. Hence, assembled structures with fluorescence properties are priceless materials for the detection of diverse analytes. The propyloxy-substituted diphenyl ether 3a demonstrated no gelation in various solvents. On the other hand, the hexyloxy- and undecyloxy-substituted diphenyl ethers 3b and 3c demonstrated good gelation properties in various solvents. The synthesized alkoxy-substituted diphenyl ether gelators consist of terminal aliphatic flexible tails and a rigid diphenyl core accountable for π-stacks. The aggregations of those diphenyl ether molecular gelators provide three-dimensional highly ordered nanofeather-like entanglements, which can be tuned by the ability to generate crystals and the extent of solubility. The synthesized organogelators (3a–c) are soluble when heated in a number of solvents. At room temperature, a soft gel was produced and observed by the “stable-to-inversion” technique as demonstrated in Figure 2. The creation of organogels from compounds 3a–c was investigated in various solvents. The CGC can be defined as the minimum gelator concentration able to generate a stable organogel after thermal treatment according to the “stable-to-inversion” technique. Different samples were prepared by decreasing the gelator concentration in the same solvent. Then, the “stable-to-inversion” procedure is applied to generate a stable organogel. Thus, the lowest gelator concentration with the ability to produce a stable organogel in the same solvent is defined as the critical gelation concentration. The CGC of hexyloxy-substituted diphenyl ether organogels was observed to be solvent-dependent in the range of 1.61–8.14 mM. The organogelator 3b showed a substantial ability to gelate various solvents like ethylacetate, n-propanol, DMSO, and n-octanol. Nonetheless, compound 3b was found to incompletely gelate other solvents like acetonitrile and toluene.
showed no gelation in ethanol, DMF, THF, 1,2-dichloroethane, CH$_2$Cl$_2$, CHCl$_3$, hexane, or benzene. The gelation properties of the diphenyl ether gelators 3a–c in a variety of solvents are summarized in Table 2. The propyloxy-substituted diphenyl ether 3a displayed low solubility. Therefore, it precipitates in various solvents. The undecyloxy-substituted diphenyl ether 3c displayed a very high solubility. Thus, it forms clear solutions in many solvents at room temperature. The formed organogels were either colorless or white soft materials. The thermal reversibility between sol and gel was highly accomplished. The generated gels showed photophysical properties almost identical to those observed for their corresponding solution states. The aliphatic tails are nonpolar groups with a single bond between carbon and hydrogen atoms. Hence, the attraction forces between those aliphatic tails are relatively weak London dispersion (van der Waals) attraction forces, which typically strengthen with increasing the aliphatic tail length due to increasing the molecular surface area. Therefore, the hexyloxy- and undecyloxy-substituted diphenyl ethers with longer alkyll tails (3b and 3c) have shown enhanced gelation properties as compared to the propyloxy-substituted diphenyl ether 3a, comprising a shorter alkyll tail.

As demonstrated in Figure 3, a blue shift was detected in the fluorescence maximum wavelength for the gel state of 3b compared to the fluorescence maximum wavelength for a diluted solution of 3b (sol state) in DMSO. This could be attributed to the formation of H-aggregates’ organogels. H-aggregations have a tendency to produce 2D nanofiber-like architectures owing to the intermolecular van der Waals attraction forces of the terminal alkyloxy groups in collaboration with intermolecular π-stacks of the diphenyl core.

Table 3 summarizes quantum yields of 3a–c in gel (or partial organogel) and solution states. The generated gels showed various fluorescence wavelengths in comparison to the sol state of a gelator. In DMSO, the sol state fluorescence of 3b at 377 nm was found to shift to 371 nm for the gel phase. The incomplete gelation showed lower shift activity in the emission wavelengths as compared to the complete gelation cases. The quantum yields of 3a and 3b increased in the gel state in comparison to the solution state.

The thermal stability of the diphenyl ether organogel 3b in octyl alcohol was studied by reporting the CGC-dependent gel → sol transition as shown in Figure 4. The gel melting point was found to increase from 38 to 49 °C when increasing the gelator concentration from 1.6 to 15.0 mmol L$^{-1}$, respectively. The enhanced thermal stability could be attributed to the high gelator density in the nanostructures. Nonetheless, the gel melting point decreased when increasing the gelator total content above 15.0 mmol/L.

The temperature-dependent transition was studied to examine the gel–sol reversibility (Figure 5). The soft gel was heated to 195 °C until it formed a colorless solution. During the heating process, the gel’s collapsing temperature was recorded. The solution-containing glass vial was then left to settle for a few minutes at 25 °C, allowing the gel to regenerate as demonstrated by the “stable-to-inversion” technique. The preceding procedures were repeated in several cycles to verify no changes in the gel → sol transition temperature, confirming excellent reversibility.

Table 2. Gelation Screening of Alkoxy-Substituted Diphenyl Ethers 3a–c in a Variety of Solvents; G = Gel; PG = Partial Gel; Sol = Solution; P = Precipitate; CGC (mM)

| solvent          | gelation screening | 3a | 3b | 3c |
|------------------|--------------------|----|----|----|
| ethylacetate     | PG                 | G  | (2.42 mM) | PG |
| THF              | Ppt                | sol| sol| sol|
| DMF              | sol                | sol| sol| sol|
| CH$_2$Cl$_2$     | sol                | sol| sol| sol|
| CHCl$_3$        | sol                | sol| sol| sol|
| n-propanol      | PG                 | G  | (8.14 mM) | PG |
| n-octanol       | PG                 | G  | (1.61 mM) | G  | (4.36 mM) |
| 1,2-dichloroethane | Ppt            | ppt| sol| sol|
| acetonitrile    | PG                 | PG | PG | PG |
| hexane          | Ppt                | Ppt| Ppt| Ppt|
| DMSO            | sol                | G  | (2.76 mM) | G  | (3.71 mM) |
| ethanol         | Ppt                | Ppt| sol| sol|
| toluene         | PG                 | PG | PG | PG |
| benzene         | Ppt                | Ppt| Ppt| Ppt|

Figure 2. Thermal and fluorescence reversibilities of organogel (3b) in DMSO under visible and ultraviolet lights.

Figure 3. Normalized fluorescence of 3b in both the gel and sol (DMSO; 2.14 × 10$^{-3}$ mol/L) phases.

Figure 4. Gelation screening of 3a–c in DMSO under visible and ultraviolet lights.

Figure 5. Gelation screening of 3a–c in DMSO under visible and ultraviolet lights.

3.4. Morphologies and Assemblies. Utilizing both SEM and TEM analyses, the morphologies of the diphenyl ether xerogels 3a–c were studied. Depending on the length of the aliphatic chain, various supramolecular morphologies were monitored, including nanofibers, nanofibers, and nanosheets. The self-assembled nanofibers of 3b were observed to be...
strongly ordered and consistent. SEM micrographs were utilized to inspect the morphological aggregations of 3b and 3c xerogels, as shown in Figures 6 and 7. The gel was dropped onto a piece of glass and left to air-dry overnight to provide xerogel. SEM images demonstrated the formation of three-dimensional self-assembled architectures due to the immobilization of solvent molecules. SEM micrographs showed highly ordered nanofeather-like supramolecular porous assemblies to indicate strong intermolecular attraction forces. Self-assembly into nanofeathers with a width in the range of 220−410 nm and a length of few microns was observed in SEM images of 3b due to immobilization of n-octanol molecules (Figure 6). On the other hand, multilayer-like supramolecular architectures (nanosheets) were observed in the SEM images of 3c upon immobilizing the n-octanol molecules (Figure 7). The morphology of 3a (partial gel) was determined after dilution in n-octanol, as shown in Figure 8. One-dimensional nanofibrous supramolecular architectures were detected for
the partial organogel generated by 3a. TEM images of 3a (partial gel) showed nanofibers with diameters of 10–19 nm and a length of few microns. Upon increasing the aliphatic tail length, the highly ordered supramolecular porous self-assembly monitored for 3b decreases to less ordered and less porous supramolecular architectures as monitored for 3c. This could be attributed to decreasing the intermolecular attraction forces when increasing the aliphatic tail length. Thus, the length of the alkoxy tail was monitored as a key element in enhancing the gelator stability.

3.5. Biological Properties. The synthesized gelators 3a—c were examined for their cytotoxicity to report the viability of BJ1 cells upon exposure to those alkoxy-substituted diphenyl ethers. Both 3a and 3b displayed no effect on cell proliferation. On the other hand, gelator 3c starts to mislay its viability, resulting in viable cells of 92.57%. Due to the precipitation tendency of organic compounds from solutions, there is less space for the growth of cells, leading to a decrease in cell numbers. Therefore, the alkoxy-substituted diphenyl ethers 3a and 3b are evidently harmless. Hence, those compounds can be possibly utilized for drug delivery purposes. Additionally, the antimicrobial activity was tested against E. coli and S. aureus, demonstrating satisfactory antibacterial performance, as summarized in Table 4. Nonetheless, the antibacterial performance decreased on extending the aliphatic tail length.

| Compound | S. aureus (%) | E. coli (%) |
|----------|--------------|-------------|
| 3a       | 17 ± 1.1     | 18 ± 1.1    |
| 3b       | 19 ± 1.0     | 22 ± 1.0    |
| 3c       | 26 ± 1.2     | 28 ± 1.4    |

4. CONCLUSIONS
A series of alkoxy-substituted iodo-biphenyl ethers able to self-assemble into nanofeather-like supramolecular architectures were synthesized and studied by various spectroscopic methods. The presence of the iodo-biphenyl moiety and alkoxy groups was monitored to gelate organic solvents into highly ordered self-assembled nanofeather-like supramolecular architectures. The suitable molecular combination of the iodo-biphenyl moiety with the terminal aliphatic tails facilitated the creation of those supramolecular architectures. The characteristic self-assembly of those alkoxy-substituted iodo-biphenyl ethers into nanostructural assemblies was inspected by SEM and TEM analysis techniques. Depending on the aliphatic chain length, different morphologies were observed, including nanofeathers, nanosheets, and nanofibers. SEM micrographs of the undecyloxy-substituted diphenyl ether xerogel showed highly ordered nanofeather-like supramolecular porous assemblies (220–410 nm) to indicate strong intermolecular attraction forces. On the other hand, multilayer-like architectures (nanosheets) were observed for the hexyloxy-substituted diphenyl ether xerogel. The morphology of the propyloxy-substituted diphenyl ether partial gel displayed one-dimensional nanofibrous supramolecular assemblies of nanofibers with diameters of 10–19 nm. The creation of nanofeathers could be ascribed to π-stacking of the iodo-biphenyl moiety in collaboration with van der Waals attraction forces of long aliphatic tails. The present alkoxy-substituted iodo-biphenyl gelators were observed to be non-cytotoxic with satisfactory antibacterial properties...

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03838.
Thermal and fluorescence reversibility of organogels under visible and ultraviolet lights and 1H NMR spectra of the compounds prepared in the study (PDF)

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Table 4. Antimicrobial Properties of Diphenyl Ethers

| Compound | S. aureus (%) | E. coli (%) |
|----------|--------------|-------------|
| 3a       | 17 ± 1.1     | 18 ± 1.1    |
| 3b       | 19 ± 1.0     | 22 ± 1.0    |
| 3c       | 26 ± 1.2     | 28 ± 1.4    |
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03838

Notes
The authors declare no competing financial interest. All relevant data are within the manuscript and available from the corresponding author upon request.

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