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## Synthesis, Thermal, and Light-Emitting Properties of Anthracene Derivatives

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*Several anthracene derivatives were prepared by a single-step reaction and characterized their thermal properties by differential scanning calorimetry (DSC) and thermogravimetric analyses. Their photoluminescence properties were examined in a large number of organic solvents of increased polarity that included toluene, chloroform, tetrahydrofuran, acetone, methanol, acetonitrile, and dimethyl sulfoxide. Some compounds exhibited emission spectra with vibrational fine structures in organic solvents; and other compounds exhibited structureless emission spectra in organic solvents.*

**Keywords:** anthracene derivatives; differential scanning calorimetry; photoluminescence; vibrational fine structures

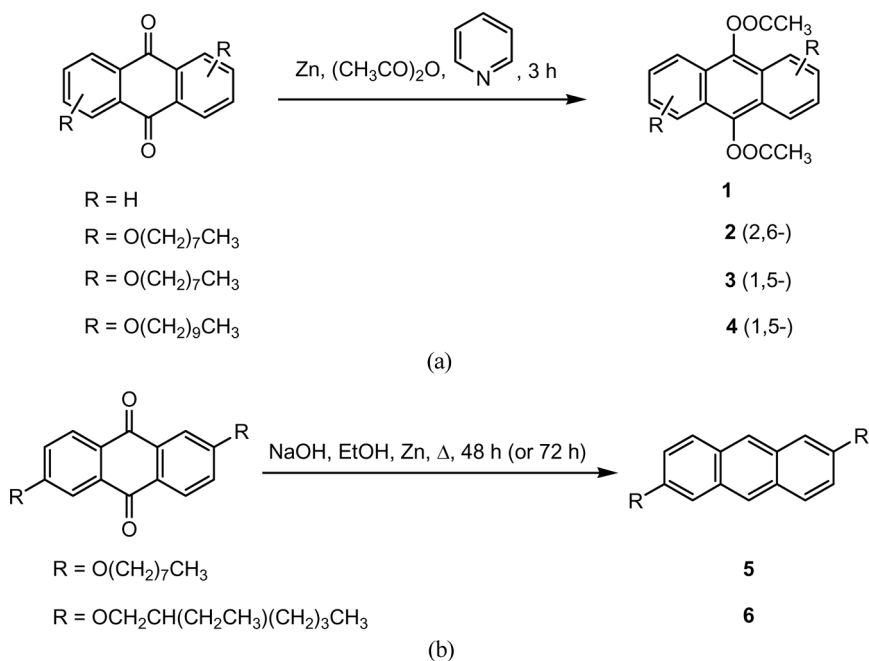
### INTRODUCTION

The properly designed anthracene derivatives are an important class of compounds that exhibit a large number of properties ranging from thermotropic liquid-crystalline to light-light emitting properties [1–4]. Even anthracene itself exhibits a high quantum efficiency of photoluminescence (0.99) in the solid state [5]. Similarly, anthracene containing polymers are also of significant interest for the development of many functional materials [6–12]. Among the numerous derivatives of anthracene, the 9,10-dihydroxyanthracene is an important compound, but because of its being prone to oxidation it is extremely difficult to purify. This difficulty poses a serious limitation to the synthesis of anthracene containing polymers

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from this compound. To overcome this problem, the 9,10-diacetoxyanthracene compound, which is a masked 9,10-dihydroxy compound, is usually used. It can be prepared via a single step from anthraquinone by using several reagents. One method uses  $\text{NaBH}_4$ /(N,N-dimethylformamide) DMF followed by in situ acetylation with acetic anhydride/pyridine yielding low yield (unspecified). However, reduction of anthraquinone with  $\text{Li}(\text{Bu}^t\text{O})_3\text{AlH}$  in bis(2-methoxyethyl)ether and then followed by in situ acetylation with acetic anhydride/pyridine gives a respectable yield of 75%, but it requires column chromatography for its purification [13]. It can also be prepared by using Zn, sodium acetate/acetic anhydride with a yield of 83% [14]. However, the polymers obtained from this compound have limited solubility in the chosen solvent of polymerization reaction that limits the molecular weights of the polymer.

In this article, we report a convenient synthesis of 9,10-diacetoxyanthracene and its isomeric dialkoxy derivatives, **1–4**, (Scheme 1) from anthraquinone and its derivatives via a single step reaction by using reductive Zn/pyridine method in presence of acetic anhydride according to the procedure reported in the literature [12], since this procedure



**SCHEME 1** (a) 9,10-diacetoxyanthracene and its derivatives; and (b) 2,6-alkoxyanthracenes.

gives an easy isolation of the desired products with excellent yields and requires no silica-gel column purification of the products. We also describe a single step procedure for the synthesis of 2,6-dialkoxyanthracenes, **5–6**, (Scheme 1) from the corresponding 2,6-dialkoxy-9,10-anthraquinones on heating to reflux in EtOH in the presence of Zn/NaOH [12]. Their chemical structures were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and elemental analyses. Their thermal and light-emitting properties in various solvents were studied by using various experimental techniques with the aim of understanding the structure-physical property relationships and developing novel materials based on these anthracene derivatives.

## EXPERIMENTAL

### General Procedure for the Preparation of Dialkoxyanthraquinone Compounds

All of these compounds were prepared by using an identical procedure as described in the literature [15]. The description for the preparation of 2,6-n-dioctyloxyanthraquinone was presented as an example. A solution of 25.0 g (104.2 mmol) of 2,6 dihydroxyanthraquinone, 132.4 g (685.7 mmol) of bromooctane, and 129.5 g (936.6 mmol) of  $\text{K}_2\text{CO}_3$  was heated to reflux in 150 mL of DMF for 12 h. After the completion of the reaction, the dark-colored solution was filtered in hot condition and the precipitate was further washed with excess DMF. The combined DMF solution containing the desired product was concentrated in a rotary evaporator. The concentrated solution was poured into 100 mL  $\text{H}_2\text{O}$  to yield the precipitate. It was then collected by filtration, washed with  $\text{H}_2\text{O}$ , and ether to give 32 g crude product. It was then recrystallized from chloroform to yield 29.0 g (62.4 mmol, yield 60%) of bright yellow crystals. It showed a  $T_m$  at 109°C (peak maximum) with  $\Delta H = 15.6$  kcal/mol (lit. [16] m.p. = 105–106°C) in the first heating cycle, and a  $T_c$  at 87°C (peak maximum) with  $\Delta H = 8.8$  kcal/mol in the first cooling cycle.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 8.21 (d, 2H), 7.71 (s, 2H), 7.20 (dd, 2H), 4.14 (t, 4H), 1.30–1.84 (m, 24H), 0.90 (t,  $J = 8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 182.25, 164.06, 135.87, 129.64, 127.01, 120.88, 110.55, 68.84, 31.83, 29.33, 29.24, 29.07, 25.98, 22.67, 14.10; Anal. Calcd (found) for  $\text{C}_{30}\text{H}_{40}\text{O}_4$  (464.65): C, 77.55 (77.48); H, 8.68 (8.32). Data for 2,6-di(2-ethylhexyloxy)anthraquinone: yield = 30% (reflux time = 60 h); recrystallized from methanol, m.p. = 70–73°C as determined by DSC at a heating rate of 10°C/min (lit. [17] m.p. = 49–51°C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 8.19 (d,  $J = 8.5$  Hz, 2H), 7.70 (s, 2H), 7.19 (d,  $J = 8.5$  Hz, 2H), 4.02 (d,  $J = 5.5$  Hz,

4H, OCH<sub>2</sub>), 1.75–1.81 (m, 2H, CH(CH<sub>3</sub>)), 1.34–1.54 (m, 16H), 0.92–0.98 (m, 12H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 182.27, 164.29, 135.88, 129.62, 127.00, 120.84, 110.64, 71.34, 39.34, 30.51, 29.08, 23.88, 23.04, 14.06, 11.12; Anal. Calcd (found) for C<sub>30</sub>H<sub>40</sub>O<sub>4</sub> (464.65): C, 77.55 (76.83); H, 8.68 (8.30). Data for 1,5-dioctyloxyanthraquinone: yield = 56% (reflux time = 4 h); recrystallized from acetone; it showed a T<sub>m</sub> at 94°C (peak maximum) with ΔH = 11.1 kcal/mol (lit. [16,18] m.p. = 89–91 and 90–92°C, respectively) in the first heating cycle and a T<sub>c</sub> at 73°C (peak maximum) with ΔH = 8.5 kcal/mol in the first cooling cycle; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 7.89 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 8 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 4.16 (t, J = 6.8 Hz, 4H), 1.30–1.96 (m, 24H), 0.90 (t, J = 6.4 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 182.56, 159.40, 137.55, 134.77, 121.14, 119.51, 117.84, 69.69, 31.84, 29.33, 29.22, 29.14, 25.96, 22.67, 14.11; Anal. Calcd (found) for C<sub>30</sub>H<sub>40</sub>O<sub>4</sub> (464.65): C, 77.55 (77.19); H, 8.68 (8.28). Data for 1,5-didecyloxyanthraquinone: yield = 49% (reflux time = 4 h); recrystallized from acetone; it showed a T<sub>m</sub> at 96°C (peak maximum) with ΔH = 17.6 kcal/mol (lit. [15] m.p. = 94–96°C) in the first heating cycle, and a T<sub>c</sub> at 76°C (peak maximum) with ΔH = 8.4 kcal/mol in the first cooling cycle. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 7.88–7.89 (dd, 2H), 7.63–7.67 (dd, 2H), 7.23–7.26 (dd, 2H), 4.16 (t, J = 6.8 Hz, 4H), 1.91–1.99 (m, 4H), 1.52–1.60 (m, 4H), 1.27–1.43 (m, 24H), 0.88 (t, J = 7.0 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm) 182.85, 159.58, 137.71, 135.04, 121.24, 119.71, 117.96, 69.85, 32.15, 29.81, 29.79, 29.60, 29.57, 29.33, 26.16, 22.93, 14.37; Anal. Calcd (found) for C<sub>34</sub>H<sub>48</sub>O<sub>4</sub> (520.76): C, 78.42 (76.83); H, 9.29 (8.30).

### General Procedure for the Preparation of Compounds 1–4

Five grams (24.0 mmol) of anthraquinone and 6.1 g (60.0 mmol) of acetic anhydride were added in a round-bottomed flask containing 20 mL of pyridine. When the temperature reached 70°C because of exothermic reaction, 2.9 g (45.0 mmol) of zinc powder was added slowly. It was then heated to reflux for 3 h. Upon completion of the reaction, the contents of the flask were allowed to cool down to rt. The reaction mixture was poured into 60 mL of dilute aqueous HCl in a beaker in which the compound was precipitated. It was collected by filtration, washed with H<sub>2</sub>O, and then recrystallized twice from chloroform to yield 4.6 g (15.6 mmol, 65%) of **1** of pale yellow crystals (lit. [13,14] m.p. = 264–266 and 279–280°C). However, the DSC thermogram of **1** obtained at a heating rate of 10°C/min did not produce any melting endotherm until decomposition temperature at ca. 233°C as determined by TGA at a heating rate of 10°C/min in

nitrogen.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 7.91–7.96 (m, 4H), 7.48–7.58 (m, 4H), 2.63 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 169.76, 140.52, 126.67, 124.32, 121.95, 21.06; Anal. Calcd (found) for  $\text{C}_{18}\text{H}_{14}\text{O}_4$  (294.31): C, 73.46 (73.18), H, 4.79 (5.15). The compounds **2–4** were prepared from the respective dialkoxy-9,10-anthraquinones instead of anthraquinone by using identical procedure to that of **1**. Data for **2**: yield = 76% (recrystallized from chloroform); it showed a  $T_m$  at 171°C (peak maximum) with  $\Delta H = 13.9$  kcal/mol in the first heating cycle and a  $T_c$  at 162°C (peak maximum) with  $\Delta H = 14.4$  kcal/mol in the first cooling cycle.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 7.76 (d,  $J = 9.6$  Hz, 2H), 7.17 (dd,  $J = 9.2$  Hz,  $J = 2.4$ , 2H), 7.00 (d,  $J = 2.4$  Hz, 2H), 4.10 (t,  $J = 6.4$  Hz, 4H), 2.61 (s, 6H), 1.31–1.86 (m, 24H), 0.91 (t,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 169.60, 157.03, 139.10, 123.89, 123.25, 122.02, 121.47, 98.67, 68.24, 32.05, 29.63, 29.49, 29.37, 26.38, 22.90, 21.02, 14.34; Anal. Calcd (found) for  $\text{C}_{34}\text{H}_{46}\text{O}_6$  (550.74): C, 74.15 (74.32); H, 8.42 (8.08). Data for **3**: yield = 79% (recrystallized from chloroform); it showed a  $T_m$  at 181°C (peak maximum) with  $\Delta H = 16.2$  kcal/mol in the first heating cycle and a  $T_c$  at 152°C (peak maximum) with  $\Delta H = 18.7$  kcal/mol in the first cooling cycle.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 7.76 (d,  $J = 9.6$  Hz, 2H), 7.17 (dd,  $J = 9.2$  Hz,  $J = 2.4$ , 2H), 7.00 (d,  $J = 2.4$  Hz, 2H), 4.10 (t,  $J = 6.4$  Hz, 4H), 2.61 (s, 6H), 1.31–1.86 (m, 24H), 0.91 (t,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 170.07, 154.98, 139.62, 126.86, 126.39, 118.44, 114.27, 105.81, 69.30, 32.05, 29.67, 29.59, 29.52, 26.26, 22.89, 21.50, 14.35; Anal. Calcd (found) for  $\text{C}_{34}\text{H}_{46}\text{O}_6$  (550.74): C, 74.15 (74.32); H, 8.42 (8.08). Data for **4**: yield = 77% (recrystallized from chloroform); it showed a  $T_m$  at 166°C (peak maximum) with  $\Delta H = 19.5$  kcal/mol in the first heating cycle and a  $T_c$  at 140°C (peak maximum) with  $\Delta H = 21.2$  kcal/mol in the first cooling cycle.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 7.76 (d,  $J = 9.6$  Hz, 2H), 7.17 (dd,  $J = 9.2$  Hz,  $J = 2.4$ , 2H), 7.00 (d,  $J = 2.4$  Hz, 2H), 4.10 (t,  $J = 6.4$  Hz, 4H), 2.61 (s, 6H), 1.31–1.86 (m, 24H), 0.91 (t,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 170.07, 154.99, 140.52, 126.86, 126.38, 118.49, 114.27, 105.80, 69.30, 32.13, 29.86, 29.80, 29.70, 29.58, 29.55, 26.25, 22.91, 21.51, 14.37; Anal. Calcd (found) for  $\text{C}_{38}\text{H}_{54}\text{O}_6$  (606.85): C, 75.21 (75.40); H, 8.97 (8.89).

## General Procedure for the Preparation of Compounds 5–6

Nine grams and sixty decigrams (20.6 mmol) of 2,6-n-dioctyloxy-9,10-anthraquinone and 4.7 g (117.8 mmol) of 10% aqueous solution NaOH were added in a round-bottomed flask containing 150 mL of ethanol.

When the contents of the reaction flask was started to reflux because of exothermic reaction, three portions of 3.6 g (55.8 mmol) of zinc powder were slowly added every 30 mins. The heating of the reflux was continued and maintained for 48 h. After the end of the reaction, the reaction flask was allowed to cool down to rt. The crude product **5** was collected by filtration and washed with water. It was then recrystallized from chloroform to yield 7.8 g (17.9 mmol, 87%) of heavy yellow crystals having melting transition at the peak maximum of 153°C with  $\Delta H = 19.5$  kcal/mol in the first heating cycle (lit. [15] m.p. = 141–143°C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 8.16 (s, 2H), 7.80 (d, 2H), 7.15 (s, 2H), 4.10 (t,  $J = 6.4$  Hz, 4H), 1.31–1.86 (m, 24H), 0.91 (t,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 155.98, 131.27, 129.13, 128.70, 124.13, 120.78, 104.62, 67.98, 31.86, 29.43, 29.28, 26.19, 22.68, 14.11; Anal. Calcd (found) for  $\text{C}_{30}\text{H}_{42}\text{O}_2$  (434.67): C, 82.90 (82.81); H, 9.74 (9.46). Compound **6** was prepared according to the procedure to that for compound **5** by using 2,6-di-2'-ethylhexyloxy-9,10-anthraquinone instead of 2,6-n-dioctyloxy-9,10-anthraquinone. However, it was then recrystallized from toluene/ethanol to give yellow crystals with a yield of 50% having melting transition at the peak maximum of 85°C with  $\Delta H = 7.3$  kcal/mol in the first heating cycle (lit. [17] m.p. = 60–62°C), despite the reaction was carried out for a long period of 72 h. Data for **6**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 8.17 (s, 2H, 9 and 10 of anthracene), 7.17 (s, 2H, 1 and 5 of anthracene), 7.14 (d,  $J = 9.4$  Hz, 2H), 3.99 (d,  $J = 5.7$  Hz, Hz, 2H,  $\text{OCH}_2$ ), 1.79–1.87 (m, 1H, alkyl), 0.92–1.62 (m, 14H, alkyl);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm) 156.22, 131.30, 129.06, 128.71, 124.09, 120.85, 104.58, 70.48, 39.44, 30.72, 29.18, 24.07, 23.10, 14.10, 11.19; Anal. Calcd (found) for  $\text{C}_{30}\text{H}_{42}\text{O}_2$  (434.67): C, 82.90 (82.63); H, 9.74 (9.44).

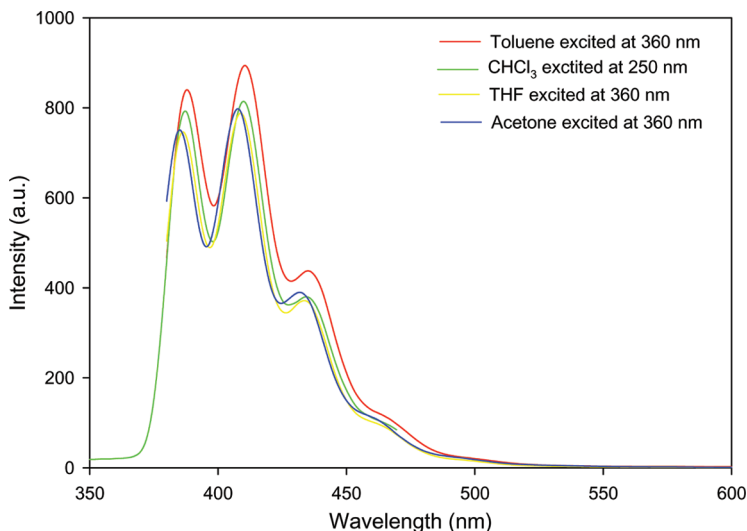
## RESULTS AND DISCUSSION

We used the  $\text{K}_2\text{CO}_3/\text{DMF}$  method in presence of alkyl bromides for the dialkylation of isomeric dihydroxyanthraquinones, which gave moderate yields and high purity without silica-gel column purification in all cases. Their m.p.s as determined by differential scanning calorimetry (DSC) were higher than the reported values in the literature [15–18]. Our yields were also comparable with the procedure that used potassium fluoride on alumina in dimethyl sulfoxide (DMSO) using *n*-octyl iodide for the alkylation reaction of isomeric dialkoxyanthraquinones. In this method, several recrystallization processes are required for the purification of each of these compounds [16]. The alkylation reaction conditions are variable and sensitive to the structures of isomeric



dialkoxyanthraquinones. The solvents typically used are DMF, DMSO, N-methylpyrrolidone (NMP), acetone, methyl ethyl ketone (MEK), chloroform, and *o*-dichlorobenzene; and the common bases used are  $K_2CO_3$ ,  $Cs_2CO_3$ , and ethyl-di-isopropylamine [3,18–20]. We successfully synthesized the compounds **1–4** by simple reductive acetylation of 9,10-anthraquinone and its isomeric dialkoxy derivatives with relatively high yields without silica-gel chromatography and characterized their chemical structures by various spectroscopic techniques and elemental analysis. There are several reagents for this type of reductive alkylation in the literature [13,14], but Zn/pyridine in presence of acetic anhydride proved to be the most effective and convenient for the synthesis of **1–4** out of which **2–4** are novel compounds. Their thermal properties were studied by thermogravimetric analysis (TGA) and DSC measurements. The TGA results revealed that all of these compounds had excellent thermal stability in the temperature range of 233–305°C, the temperature at which the 5 wt% loss of each of these compounds occurred at a heating rate of 10°C/min in nitrogen.

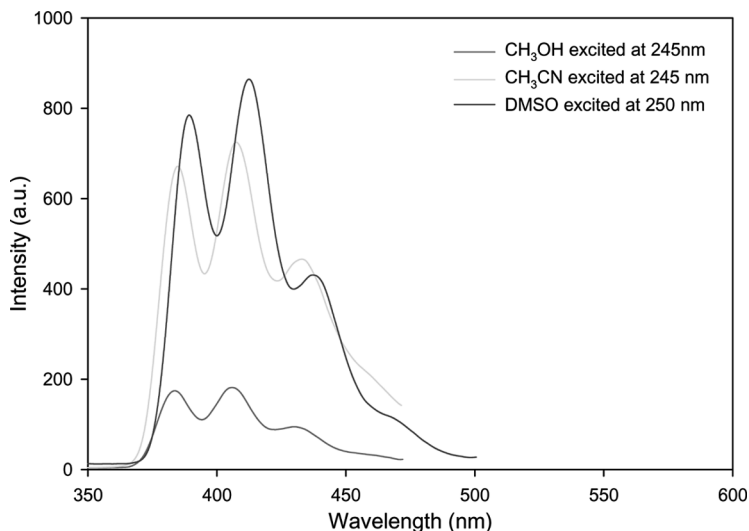
We also synthesized isomeric 2,6-dioctyloxyanthracene **5–6** from the corresponding dioctyloxyanthraquinones by using the reagent Zn/NaOH in EtOH. These compounds were also purified by simple recrystallization from chloroform and toluene/ethanol, respectively. The various reagents are typically used for the reduction of anthraquinone and its derivatives to anthracene and anthracene derivatives, which suggest that this reduction is sensitive to the substituent(s) present in the anthraquinone moiety. The notable reagents are excess  $NaBH_4$  [20–23], or complicated sodium borohydride-metal (Li or Na)-ammonia/*p*-chloroanil [24] in a stepwise procedure. One-step reductive systems of  $Al(Hg)/NH_4OH/EtOH$  (aq) [19], Zn/aqueous  $NH_3$  [25–28], Zn/NaOH (aq) [29], Zn/cyclohexyl-*p*-toluenesulfonate/hot trichlorobenzene [30], Zn/AcOH [31,32],  $SnCl_2/conc. HCl$  [25] and  $Et_3SiH/BF_3 \cdot Et_2O$  [20], are also reported for the preparation of various derivatives of anthracenes. However, the excess of  $NaBH_4$  in isopropanol is the most common method in a stepwise procedure among all the reducing reagents. In many instances, the reduction products are purified by silica-gel chromatography. Recently, the reduction of anthraquinone to anthracene is also carried out successfully in supercritical 2-propanol in presence of sulfur under argon [33]. By using Zn/NaOH/EtOH, the compounds **5** and **6** were successfully prepared by simple recrystallization with high purity, since their m.p.s as determined by DSC were higher than those reported in the literature [15,17]. Compound **5** exhibited two low-temperature endotherms in addition to its melting transition in its DSC thermograms. In contrast,



**FIGURE 1** Emission spectra of **1** in organic solvents of varying polarities ranging from  $\epsilon = 2.4$  to 20.56.

compound **6** only exhibited melting transition in its DSC thermogram, which was much lower than that of compound **5** because of the branched 2-ethylhexyl group present in **6**.

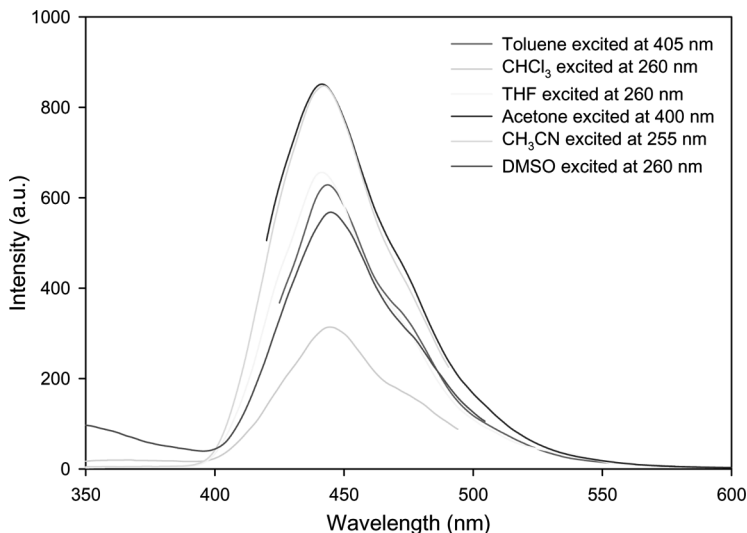
Figure 1 shows the photoluminescence spectra of compound **1** in organic solvents of varying polarities having the range of dielectric constants from 2.4 (toluene) to 20.56 (acetone). Each emission spectrum in each of these solvents examined has several  $\lambda_{\text{em}}$  peaks at 388, 410, 435, 465 nm when excited at 360 nm; even in  $\text{CHCl}_3$  when excited at 250 nm, its emission spectrum exhibited identical  $\lambda_{\text{em}}$  peaks. Its photoluminescence spectra exhibited fine vibrational structures similar to those observed in anthracene itself in nonpolar solvents. Its excitation spectra when monitored at ca. 410 nm in toluene, THF, acetone, and DMSO also exhibited fine structures similar to those in anthracene itself in nonpolar solvents. However, it exhibited a prominent  $\lambda_{\text{ex}}$  peak at 248 nm along with several minor  $\lambda_{\text{ex}}$  peaks when monitored at 410 nm in  $\text{CHCl}_3$  (not shown). Its several photoluminescence spectra in still higher polar solvents of both protic and aprotic types are shown in Fig. 2. In acetonitrile and DMSO, it also showed vibrational fine structures with  $\lambda_{\text{em}}$  peaks shifted bathochromically to 390, 412, 438, 467 nm when excited at 245 and 250 nm, respectively. In methanol, when excited at 245 nm, its emission spectrum remained essentially identical to those in other relatively



**FIGURE 2** Emission spectra of **1** in organic solvents of varying polarities ranging from  $\epsilon = 32.6$  to 48.9.

nonopolar solvents. Its excitation spectra also showed vibrational fine structures in these two solvents. However, its excitation spectra in both methanol and acetonitrile when monitored at 405 and 408 nm, respectively, remained essentially identical to that in  $\text{CHCl}_3$  exhibiting a major  $\lambda_{\text{ex}}$  peak at ca. 248 nm along with several minor  $\lambda_{\text{ex}}$  peaks. Generally, the vibrational fine structures in the emission spectrum of a compound are related to its rigid structure [34]. Thus, it was found that the attachment of diacetate groups in **9** and **10** positions did not change the rigidity of anthracene moiety in this compound.

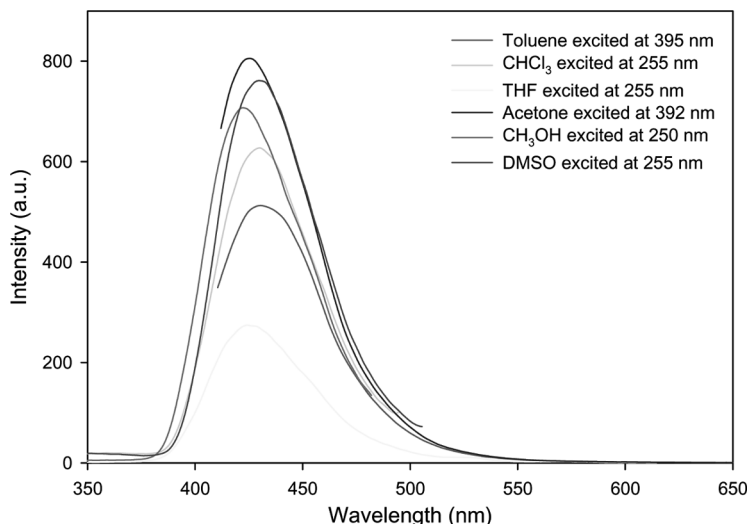
Figure 3 shows the emission spectra of compound **2** in various solvents ranging from highly nonpolar to highly polar solvent. In contrast to the emission spectra of **1**, it showed a broad  $\lambda_{\text{em}}$  at ca. 440 nm with a minor shoulder peak at low energy end of the spectrum in all of the solvents tested, despite the various excitation wavelengths used for the measurements of light emission in these solvents. However, its excitation spectra showed fine vibrational structures in some solvents (for example, toluene, THF, and acetone), but not in other solvents such as chloroform, acetonitrile, and DMSO (not shown). The loss of vibrational fine structures in the emission spectrum of **2** is presumably related to the attachment of two flexible *n*-octyloxy groups in **2** and **6** positions. In contrast, compounds **3** and **4** also exhibited both emission spectra with fine vibrational structures and excitation spectra with



**FIGURE 3** Emission spectra of **2** in organic solvents of varying polarities ranging from  $\epsilon = 2.4$  to 48.9.

fine vibrational structures in these organic solvents (not shown). Therefore, the emission spectra of 9,10-diacetate derivatives of anthracene were dependent on the location of dialkyl substituents attached to the anthracene moiety (2, 6 versus 1, 5). These results are in excellent agreement with those of other anthracene derivatives where emission spectra are dependent on the location of substituents and on the nature of the solvents [15].

Figure 4 shows the emission spectra of compound **5** in various solvents ranging from highly nonpolar solvent toluene to highly polar solvent dimethyl sulfoxide. In each of these solvents, its emission spectrum showed a broad  $\lambda_{\text{em}}$  peak at ca. 424 nm (in THF, acetone, and methanol) without displaying any vibrational fine structures, unlike the emission spectrum of anthracene in nonpolar solvents. In nonpolar solvents, its  $\lambda_{\text{em}}$  peak was shifted hypsochromically to ca. 428 nm; and in acetonitrile and DMSO, peak was shifted bathochromically to a slight extent. However, its excitation spectrum showed fine vibrational structures in some solvents (for example, toluene, THF, and acetone), but not in other solvents such as chloroform, methanol, acetonitrile, and DMSO (not shown). Similarly, compound **6** also exhibited essentially identical emission spectra with the loss of fine vibrational fine structures in these various solvents. These results are in excellent



**FIGURE 4** Emission spectra of **5** in organic solvents of varying polarities ranging from  $\epsilon = 2.4$  to 48.9.

agreement with the emission spectrum of 2,6-didecyloxyanthracene recorded in a nonpolar solvent, methyl cyclohexane [15].

When the  $\lambda_{\text{em}}$  peak of **5** compared with that of **2** it was found that the emission peak was shifted hypsochromically in various solvents, which is presumably due to the conjugation effect of diacetate groups present in compound **2**.

## CONCLUSIONS

We presented an easy synthetic procedure for the preparation of both isomeric dialkoxy-9,10-anthraquinone diacetate including 9,10-anthraquinone diacetate and isomeric dialkoxyanthracene. Their purity was of high grade, since their melting transitions were higher than the previous reported ones as determined by DSC measurements [15,17]. They had excellent thermal stability in the temperature range of ca. 233–305°C in nitrogen. They exhibited photoluminescence properties in a wide number of organic solvents. The anthracene derivatives are a novel class of light-emitting materials that have strong potential for the development of optoelectronic devices in near future.

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