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Synthesis of tetra-oligothiophene-substituted calix[4]arenes and their optical and electrochemical properties

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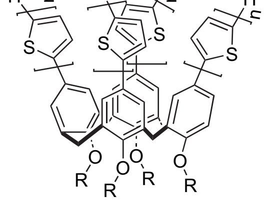
Abstract—A facile and efficient approach to synthesize tetra-oligothiophene-substituted calix[4]arenes, **Calix-OT(*n*)** with *n* up to 4 using palladium-catalyzed Kumada coupling of thienylmagnesium bromide and bromo-substituted calix[4]arene as a key step has been developed. The close proximity of the tetra-oligothiophenes constructed within a calix[4]arene assembly leads to peak/band broadening, spectral shifting, i.e., blue-shift in absorption and red-shift in emission spectra as well as fluorescence quantum yield quenching as compared to those of monomers indicating the existence of chromophoric interaction. We have shown that the intra-chromophoric interaction lowers the first ionization (raises HOMO level) of an oligothiophene within an assembly. It also stabilizes the formation of a radical cation, which results in an increase in the subsequent voltammetric oxidation and the occurrence of the higher oxidation states as compared to the monomeric counterparts. This assembly can serve as a model for the investigation of molecular interaction of π-conjugated systems.

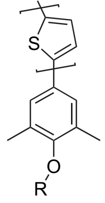
1. Introduction

Oligothiophenes are an important class of π-conjugated organic materials that have been extensively investigated and explored as active materials for (opto)electronic device applications such as field-effect transistors, light emitting diodes, photovoltaic cells, and sensors in the last few years.[1] Tuning the molecular properties of oligothiophenes by means of chemical and structural modifications has been successfully much achieved in recent years.[2] However, the ultimate bulk performance of an oligothiophene-based material relies greatly on the molecular/chain arrangement in the solid-state and/or morphology of the material.[3] For example, ordered close packing of sexithiophenes in the solid-state leads to low photoluminescence efficiency due to excitonic coupling of proximate oligomers.[4] On the other hand, proper molecular alignment results in better charge transport and lowers operating voltages in field-effect transistor applications.[5] As a result, structural studies of oligothiophenes and morphological investigations of these materials are important issues related to their applications. Toward this end, it is of great interest to investigate well-defined multi-oligothiophene-based molecular assemblies, in which thiophene oligomers are preorganized and preoriented within a molecular framework, within which studies would provide insight into the effect of through-space interactions of oligomeric and polymeric chains. Several cyclophane-based oligothiophene assemblies have been synthesized and investigated for π-stacking effects.[6] In addition, the intramolecular interaction and corporation effect of the proximate chromophores could give rise to novel or enhanced functional and structural/morphological properties of resulting materials.[7]

Calixarenes are one of the most useful building platforms for constructing supramolecular systems and have been widely used in the preparation of artificial receptors for neutral and ionic molecules.[8] One of the unique features of these calix[4]arene derivatives is that they can exist in a relatively rigid and stable cone structure, in which four functionalized phenolic units, oriented in the same direction are linked at their *ortho*-positions by methylene bridges. With oligothiophenes built onto such frameworks, the arrangement and orientation of oligothiophenes will be predefined and preorganized with the oligothiophene units close enough to interact. Thus, the effect of coupling interactions on various functional properties of such assemblies could readily be probed. We herein report the facile and efficient synthesis and optical and electrochemical properties of a novel series



Calix-OT(*n*), *n* = 1-4



M-OT(*n*), *n* = 1-4

Keywords: Tetra-oligothiophene-substituted calix[4]arene; Intra-chromophoric interaction; Kumada coupling.

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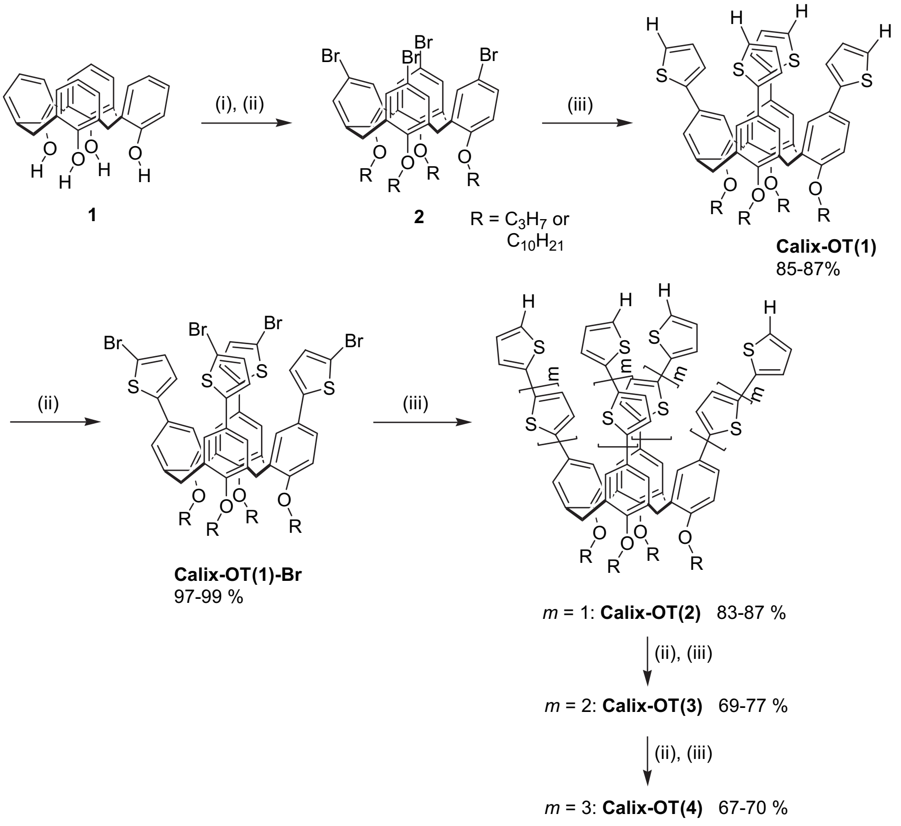
of monodisperse and well-defined π-conjugated tetra-oligothiophene-substituted calix[4]arene assemblies, **Calix-OT(*n*)** where n=1–4.

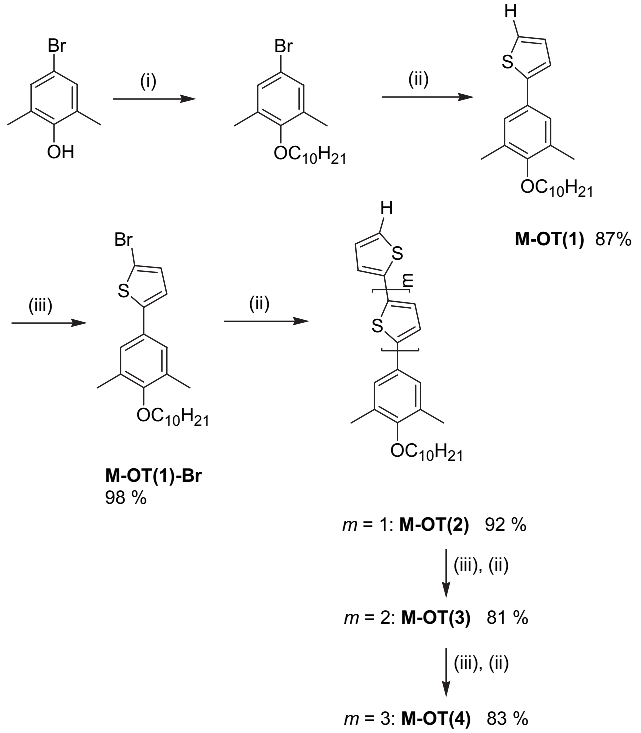
2. Results and discussion

Recently, various oligophenylene-substituted calix[4]arenes have been efficiently synthesized by palladium-catalyzed Suzuki cross-coupling reactions;[7b,c] however, such protocols were found to be not useful for the synthesis of tetra-oligothiophene-substituted calix[4]arenes, **Calix-OT(*n*)**. Even though bis(dithienyl)-substituted calix[4]arenes were previously prepared by Stille cross-coupling reaction,[1e] we find that palladium-catalyzed Kumada cross-coupling is more efficient and useful for the synthesis of tetra-oligothiophene-substituted calix[4]arenes. Since the preparations of oligothienylmagnesium bromides were non-trivial and inefficient, the use of convergent approach to synthesize the higher homologous was not practical. As a result, the tetra-oligothienyl chains were constructed onto the calix[4]arene framework by a divergent approach using palladium-catalyzed Kumada cross-coupling of thienylmagnesium bromide and tetrabromo(oligothienyl)-calix[4]arene as a key step for chain length extension. The synthetic route is outlined in Scheme 1. To stabilize the cone conformation, calix[4]arene **1** was alkylated with either bromopropane or bromodecane using NaH as a base in DMF.[9] Bromination of tetraalkoxycalix[4]arene with NBS in refluxing $CHCl_3$ afforded the tetrabromocalix[4]arene **2**.[7a] Cross-coupling of freshly prepared thienylmagnesium bromide and **2** in the presence of $PdCl_2$(dppf) as a catalyst afforded tetrathienylcalix[4]arene, **Calix-OT(1)** in a good yield (85–87%). Bromination of tetrathienylcalix[4]arene with NBS in refluxing CH_2Cl_2 gave tetrabromothienylcalix[4]arene, **Calix-OT(1)-Br** in an excellent yield (90–93%). Subsequent cross-coupling reaction of **Calix-OT(1)-Br** with thienylmagnesium bromide afforded tetrakis-(bithienyl)calix[4]arene, **Calix-OT(2)** in 83–87% yield. By repeating such a sequence of bromination and cross-coupling reactions, a higher homologue series of oligothiophene-substituted calix[4]arenes including **Calix-OT(3)** and **Calix-OT(4)** were readily synthesized. The MALDI-TOF mass spectra of **Calix-OT(3)** and **Calix-OT(4)** showed a base peak at *m/z* 1970.6421 and 2299.6157, corresponding to [M^+] and [M^++H], respectively. In addition to low/high-resolution mass spectroscopy, all the newly synthesized oligothiophene-substituted calix[4]arenes were fully characterized by ^1H NMR, ^{13}C NMR, and/or elemental analyses and found to be in good agreement with the expected structures. For properties comparison, their corresponding monomers oligothiophene-substituted 4-alkyoxy-3,5-dimethylbenzenes, **M-OT(*n*)** with n up to 4 were also synthesized using the same strategy as shown in Scheme 2.

Figure 1 shows the single crystal X-ray structure of **Calix-OT(2)**, which adopts a pinched cone structure similar to other arylene-substituted calix[4]arenes.[10] In contrast to the biphenylene counterparts, all the bithiophene units are in an *anti* coplanar conformation except there is a twist



Scheme 1. Synthesis of oligothiophene-substituted calix[4]arene assemblies, **Calix-OT(*n*)**, n=1–4. Reagents and conditions: (i) NaH, C_3H_7Br or $C_{10}H_{21}Br$, DMF, 50 °C; (ii) NBS, $CHCl_3$ or CH_2Cl_2, reflux; (iii) (a) 2-bromothiophene, Mg, THF, reflux and (b) $PdCl_2$(dppf), reflux.



Scheme 2. Synthesis of monomeric oligothiophenes, **M-OT(*n*)**, $n=1–4$. Reagents and conditions: (i) NaH, $C_{10}H_{21}Br$, DMF, 50 °C; (ii) (a) 2-bromothiophene, Mg, THF, reflux and (b) $PdCl_2(dppf)$, reflux; (iii) NBS, $CHCl_3$ or CH_2Cl_2, reflux.

between the aryl ring of calix[4]arene skeleton and bithiophene. Although the two parallel bithiophene units are leaned toward each other, the distal terminal thiophene rings do not pack in a co-facial arrangement owing to the *anti* conformation of bithiophene.

The thermal behavior and stability of these oligothiophene-substituted calix[4]arenes were investigated by DSC and TGA analyses, respectively. The results are summarized in Table 1. In general, **Calix-OT(*n*)** shows an excellent and enhanced thermal stability with T_d>400 °C than that of the corresponding **M-OT(*n*)**. All the oligothiophene-substituted calix[4]arenes are highly soluble in common organic solvents except **Calix-OT(4)**.

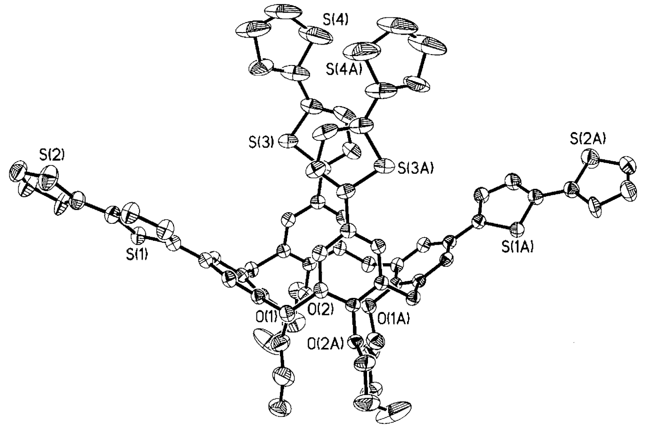


Figure 1. ORTEP drawings of **Calix-OT(2)** (25% probability). All hydrogen atoms are omitted for clarity.

The electronic absorption and emission spectra of all the oligomers, **M-OT(*n*)** and assemblies, **Calix-OT(*n*)** were recorded in chloroform and their results are summarized in Table 1. In general, there is a sequential increase in the absorption maxima with a concomitant increase in molar absorptivity and the emission maxima in both series as the thienyl unit increases. However, in addition to the peak broadening, the absorption spectra of oligothiophene-substituted calix[4]arenes are relatively blue-shifted ($\Delta=3–8$ nm) whereas their emission spectra are shifted to the longer wavelengths ($\Delta=12–14$ nm) as compared to those of corresponding monomer (Fig. 2). In contrast to the monomeric series, the moderate increase in the fluorescence quantum yield as the chain length extends was not observed in oligothiophene-substituted calix[4]arene series. All these phenomena suggest the occurrence of the chromophoric interaction of proximate tetra-thiophene oligomers constructed within the calix[4]arene framework. The blue-shift in absorption spectra can be explained in terms of the excited state splitting due to the exciton coupling of the proximate chromophores within the assembly in which the singlet–singlet transitions

Table 1. Summaries of physical measurements of **Calix-OT(*n*)** and **M-OT(*n*)** series

	λ_{max}^{abs} [a]/nm ($\varepsilon_{max}\times10^4$/$M^{-1}$ cm^{-1})	λ_{max}^{em} [a,b]/nm	Φ_{FL} [a,c]	FL lifetime in solution/ns[a,d]	E_{ox}[e]/V	T_m[f] (T_d[g])/°C
M-OT(1)	286 (1.97)	385, 402	[h]	1.03	0.87 (ir, 1e)	(292)
M-OT(2)	348 (2.71)	396, 414	0.07	1.19	0.63 (ir, 1e)	63 (352)
M-OT(3)	384 (3.54)	442, 469	0.15	1.17	0.47 (r, 1e), 0.76 (q, 1e)	112 (396)
M-OT(4)	414 (4.64)	477, 510	0.31	1.36	0.37 (r, 1e), 0.67 (r, 1e)	177 (427)
Calix-OT(1)	288 (8.02)	402, 425	[h]	1.20	0.75 (ir, 1e)	239 (412)
Calix-OT(2)	342 (8.80)	427	0.08	1.87	0.47 (ir, 1e), 0.61 (ir, 1e)	241 (409)
Calix-OT(3)	381 (12.9)	454, 482	0.11	1.77	0.44 (ir, 1e). 0.87 (q, 2e)	200 (431)
Calix-OT(4)	406 (14.8)	489, 524	0.11	1.50	0.38 (q, 1e), 0.73 (q, 2e)	227 (421)

[a] Measured in $CHCl_3$.

[b] Excited at the absorption maxima.

[c] Using quinine in 0.1 M H_2SO_4 ($\Phi_{365}=0.54$) as a standard.

[d] Estimated using an iterative fitting procedure from the measured fluorescence decayed excited by nitrogen laser.

[e] E_{ox} estimated by CV method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution and all the potentials were calibrated with ferrocene, which was also used as an internal standard, $E_{1/2}$ (Fc/Fc^+)=0.49 V versus SCE with a scan rate of 100 mV/s.

[f] Determined by differential scanning calorimeter with a heating rate of 10 °C/min under N_2.

[g] Determined by thermal gravimetric analyzer with a heating rate of 10 °C/min under N_2.

[h] Less than 0.01.

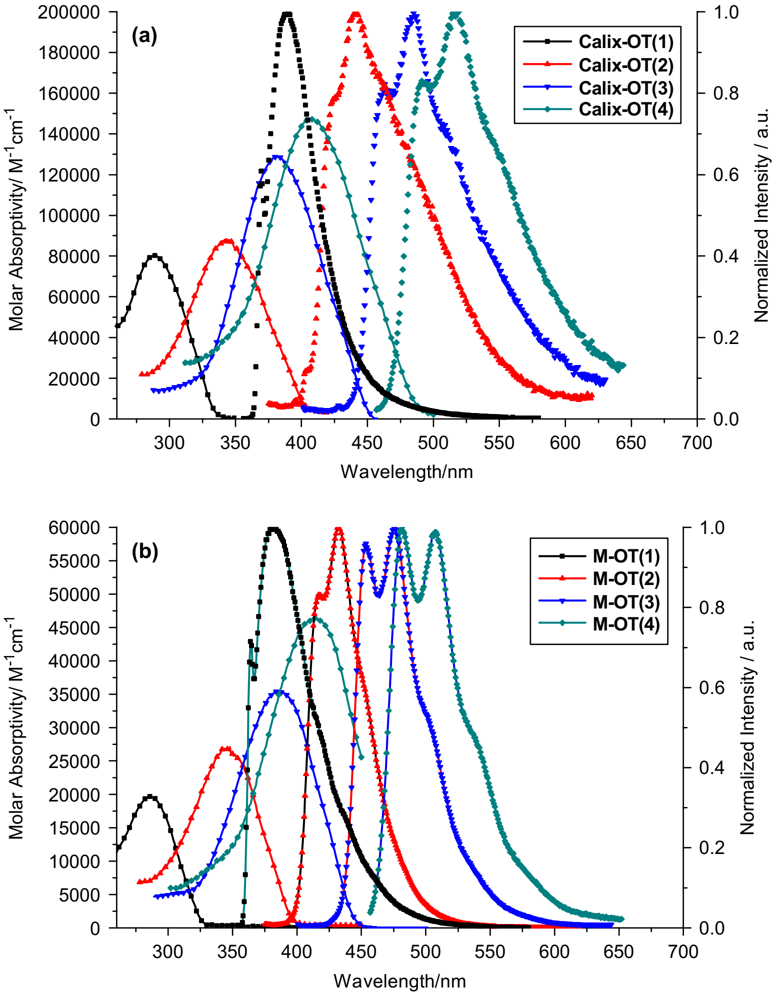


Figure 2. Absorption and emission spectra of (a) **Calix-OT(*n*)** and (b) **M-OT(*n*)** series.

from the ground state to the lowest coupled excited state are forbidden but to the second excited state are allowed.[11] Because of the through-space interaction and/or the steric shielding imposed by proximate oligomers, the oligothiophene-substituted calix[4]arenes exhibit slightly longer fluorescence lifetimes (1.20–1.87 ns) than the corresponding monomeric counterparts (1.03–1.36 ns).

The redox properties of **M-OT(*n*)** and **Calix-OT(*n*)** were studied by cyclic voltammetry, which was carried out in a three-electrode cell set-up with 0.1 M of Bu_4NPF_6 as supporting electrolyte in $CHCl_3$. All the potentials reported are internally referenced to Fc/Fc^+ standard and the results are tabulated in Table 1. **M-OT(1)** exhibits an irreversible one-electron oxidation with E_{pa} at 0.87 V in $CHCl_3$ corresponding to the formation of monocation. When repeated cycling of the electrode between 0 and 1.8 V, an appearance of solid films on the electrode surface and a growing broad wave at a lower potential associated with an increased peak current were observed indicating the occurrence of electrochemical dimerization/polymerization. As the thienyl unit increases, the first oxidation potential decreases progressively. Furthermore, there is an improvement in reversibility of the voltammetric wave and instability toward electrochemical reactions as the chain length increases. In contrast to **M-OT(1)** and **M-OT(2)**, the voltammetric wave of **M-OT(3)** and **M-OT(4)** also exhibits two one-electron oxidation waves corresponding to the sequential formation of monocation and dication. The second oxidation potential also decreases with an increase in thienyl unit. All these evolution/changes are attributed to the stabilizing effect of the enhanced π-conjugation of the longer homologues.

Even though there were several reports on the electrochemical studies of polythiophene–calixarene hybrid materials,[1e,12] the electrochemical properties of tetra-oligothiophene–calixarene molecules are not known. The influence of intramolecular chromophoric interaction on the electrochemical properties of **Calix-OT(*n*)** is profound. Even though **Calix-OT(1)** exhibits an irreversible one-electron oxidation similar to **M-OT(1)**, its oxidation potential (E_{pa}=0.75 V) is substantially lower than that of **M-OT(1)** (E_{pa}=0.87 V). The lowering of the first oxidation potential of **Calix-OT(*n*)**s relative to **M-OT(*n*)**s is consistently observed throughout the series. This phenomenon suggests that the cation formed is stabilized by the proximate thiophene oligomers within the assembly. In addition, the intra-chromophoric stabilization leads to the exhibition of two well-resolved one-electron oxidation waves of **Calix-OT(2)** corresponding to the sequential formation of monocation and dication whereas

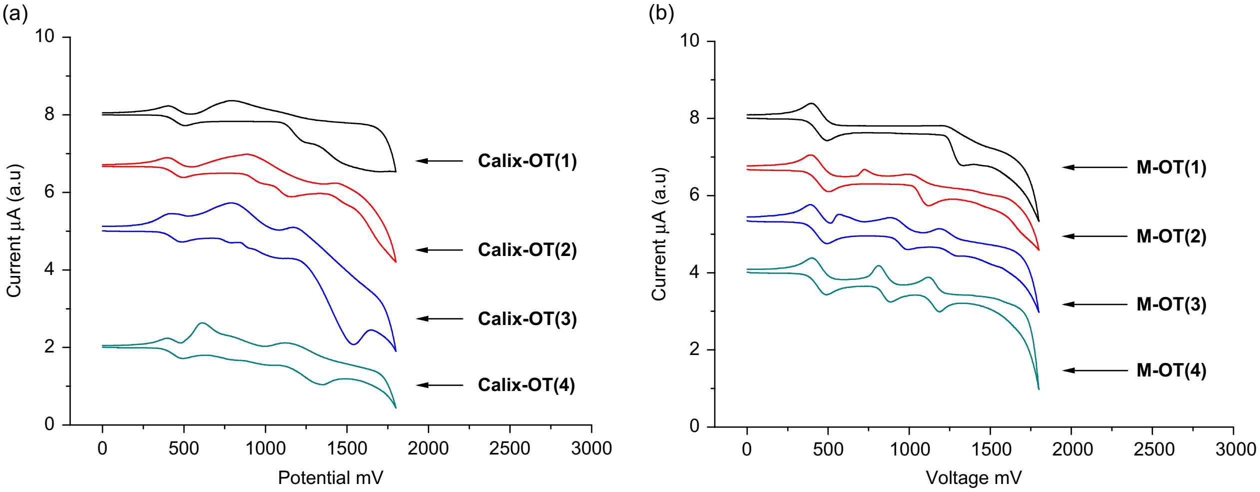


Figure 3. CV traces of (a) **Calix-OT(*n*)** and (b) **M-OT(*n*)** series with ferrocene were used as an internal standard, $E_{1/2}$ (Fc/Fc$^+$)=0.49 V versus SCE with a scan rate of 100 mV/s.

M-OT(2) only exhibits a single one-electron oxidation (Fig. 3). The stabilizing effect imposed by proximate oligomers and chain length extension also leads to the exhibition of the higher oxidation states in **Calix-OT(3)** and **Calix-OT(4)**. There are small steps appearing in the oxidation waves of the higher homologues, which are attributed to the micro-environment difference for each thiophene oligomer within an assembly. Such a difference is likely created by the relatively slow interconversion of two conformationally mobile C_{2v} 'pinched or flattened' cone conformers in solution for the higher homologues within CV time scale. On the other hand, **Calix-OT(3)** appears to have a higher second oxidation potential than that of **Calix-OT(2)**, which is attributed to one more electron involved in the second oxidation of **Calix-OT(3)**. For **Calix-OT(4)**, the second oxidation potential drops again. Since the number of electrons involved in the second oxidation of **Calix-OT(3)** and **Calix-OT(4)** is more, their second oxidation generally occurs at a higher potential than that of the corresponding **M-OT(*n*)**. Electro-polymerization also occurs readily for the **Calix-OT(*n*)** series upon repeated anodic scans.

3. Conclusions

In summary, we have developed a divergent approach to synthesize a novel series of tetra-oligothiophene-substituted calix[4]arenes, **Calix-OT(*n*)** with *n* up to 4 by means of a facile and efficient palladium-catalyzed Kumada coupling of thienylmagnesium bromide and bromo-substituted calix[4]arene as the key step. In addition to the spectral widening, blue-shift of absorption spectra, red-shift of emission spectra, and increased quenching in fluorescence quantum yields, the intramolecular coupling/interaction leads to lowering of the first oxidation potential of an oligothiophene stabilizing the formation of radical cation and exhibiting higher oxidation states in higher homologues of the tetra-oligothiophene-substituted calix[4]arenes assembly. These assemblies can serve as a model in the intermolecular interaction of π-conjugated molecules/polymers. Our studies also provide an insight into the influence of intermolecular interaction on the positive charge in the condensed phase.

4. Experimental

4.1. General

All the solvents were dried by the standard methods wherever needed. ^{1}H NMR spectra were recorded using a 270 MHz or 400 MHz FT-NMR spectrometer and are referenced to the residual $CHCl_3$ 7.24 ppm. ^{13}C NMR spectra were recorded using a 270 MHz or 400 MHz FT-NMR spectrometer and are referenced to the $CDCl_3$ 77 ppm. High-resolution mass spectroscopy (HRMS) measurement was carried using MALDI-TOF method. The fluorescence decay curves were recorded on PTI fluorescence Master 2M1 Luminescence Spectrophotometer using PTI G2-3300 Nitrogen Laser as excitation. The lifetimes were estimated from the measured fluorescence decay using iterative fitting procedure. $E_{1/2}$ (E_{pa}) versus Fc$^+$/Fc was estimated by cyclic voltammetric method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution (1 mM) dissolved in $CHCl_3$ using 0.1 M of Bu_4NPF_6 as a supporting electrolyte with a scan rate of 100 mV/s and all the potentials were calibrated and referenced with ferrocene ($E_{1/2}$ (Fc/Fc$^+$)=0.49 V vs SCE) as an internal standard.

4.1.1. 5,11,17,23-Tetrakis(thienyl)-25,26,27,28-tetrapropoxycalix[4]arene Calix-OT(1). To a flame dried 100-mL two-necked flask containing 2-bromothiophene (0.7 g, 4.3 mmol) in 20 mL anhydrous THF were added Mg turnings (0.12 g, 5 mmol) at room temperature under N_2. The solution mixture was stirred vigorously. After the boiling had stopped, the reaction mixture was heated to reflux for 3 h. After cooling to room temperature, tetrabromocalix[4]arene **2** (0.2 g, 0.22 mmol) and $PdCl_2$(dppf) (9 mg, 5 mmol %) were added and allowed to reflux overnight. After cooling, the reaction mixture was quenched with 50 mL of water, acidified with 6 M HCl to pH 4–5 and then extracted with DCM (3×20 mL). The combined organic solvent was washed with brine and dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by flash silica gel column chromatography using petroleum ether as eluent affording the title compound as a white solid (0.17 g, 85% yield). ^{1}H NMR (270 MHz, $CDCl_3$, δ) 6.98 (t, J=3.2 Hz, 4H), 6.92 (s, 8H), 6.78 (d, J=3.5 Hz, 8H), 4.47 (d, J=13.2 Hz, 4H), 3.89 (t, J=7.6 Hz, 8H), 3.20 (d, J=13.2 Hz, 4H), 1.96–1.94 (m, 8H), 1.00 (t, J=4.9 Hz, 12H). ^{13}C NMR (67.5 MHz, $CDCl_3$, δ) 156.1, 144.4, 135.0, 128.5, 127.5, 125.9, 123.4, 121.8, 76.9, 31.1, 23.3, 10.5. MS (FAB) *m/z* 920.6 [M$^+$]. Anal. Calcd for $C_{56}H_{56}O_4S_4$: C, 73.01; H, 6.13. Found: C, 72.89; H, 6.12.

4.1.2. 5,11,17,23-Tetrakis(5-bromothienyl)-25,26,27,28-tetrapropoxycalix[4]arene Calix-OT(1)-Br. To a stirred solution of **Calix-OT(1)** (0.22 g, 0.24 mmol) in 30 mL CH_2Cl_2 in a 100-mL round-bottomed flask was added NBS (0.17 g, 0.96 mmol). The solution mixture was heated to reflux overnight. After evaporating the solvent, the residue was purified by flash silica gel column chromatography using CH_2Cl_2 as eluent affording a white solid (0.27 g 90% yield). ^{1}H NMR (270 MHz, $CDCl_3$, δ) 6.81–6.79 (m, 12H), 6.55 (d, J=3.8 Hz, 4H), 4.45 (d, J=13.2 Hz, 4H), 3.86 (t, 8H), 3.16 (d, J=13.2 Hz, 4H), 1.93–1.88 (m, 8H), 0.99 (t, 12H). ^{13}C NMR (67.5 MHz, $CDCl_3$, δ) 156.4, 145.7, 135.2, 130.5, 127.7, 125.3, 121.9, 77.2, 31.1, 23.3, 10.4. MS (FAB) *m/z* 1236.2 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{56}H_{53}Br_4O_4S_4$: 1236.9527. Found: 1236.9569 [M$^+$+H].

4.1.3. 5,11,17,23-Tetrakis(dithienyl)-25,26,27,28-tetrapropoxycalix[4]arene Calix-OT(2). The coupling procedure described above was followed using 2-bromothiophene (0.8 g, 4.9 mmol), Mg turnings (0.14 g, 5.8 mmol), **Calix-OT(1)-Br** (0.3 g, 0.24 mmol), and $PdCl_2$(dppf) (9 mg, 5 mmol %). The crude product was purified by flash silica gel column chromatography using CH_2Cl_2/petroleum ether (v/v=1/3) as eluent affording a pale yellow solid (0.25 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.10 (d, J=1.2 Hz, 4H), 7.01 (d, J=3.6 Hz, 4H), 6.93 (s, 8H), 6.92–6.89 (m, 4H), 6.80 (d, J=3.6 Hz, 4H), 6.71 (d, J=3.2 Hz, 4H), 4.49 (d, J=13.6 Hz, 4H), 3.90 (t, J=7.2 Hz, 8H), 3.22 (d, J=13.6 Hz, 8H), 1.99–1.93 (m, 8H), 1.02 (t, J=7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.4, 143.3, 137.8, 135.3, 135.2, 128.3, 127.6, 125.6, 124.4, 123.6, 123.0, 122.5, 76.9, 31.0, 23.2, 10.3. MS (FAB) *m/z* 1248.8 [M$^+$]. Anal. Calcd for $C_{72}H_{64}O_4S_8$: C, 69.19; H, 5.16. Found: C, 69.08; H, 5.14.

4.1.4. 5,11,17,23-Tetrakis(5′-bromodithienyl)-25,26,27,28-tetradecyloxycalix[4]arene Calix-OT(2)-Br. The bromination procedure described above was followed using **Calix-OT(2)** (0.16 g, 0.1 mmol) and NBS (69.5 mg, 0.4 mmol). The crude product was purified by flash silica gel column chromatography using CH_2Cl_2/petroleum ether (v/v=1/3) as eluent affording a white solid with a quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.91 (s, 8H), 6.87 (d, J=3.2 Hz, 4H), 6.77 (s, 4H), 6.74 (d, J=3.6 Hz, 8H), 4.48 (d, J=13.2 Hz, 4H), 3.93 (t, J=7.2 Hz, 4H), 3.21 (d, J=13.2 Hz, 4H), 1.93–1.92 (m, 8H), 1.39–1.29 (m, 56H), 0.89 (t, J=6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.6, 143.8, 139.2, 135.3, 134.4, 130.4, 128.0, 125.6, 124.5, 122.9, 122.5, 110.2, 75.5, 32.0, 31.0, 30.3, 30.0, 29.9, 29.8, 29.5, 26.4, 22.7, 14.1. MS (FAB) *m/z* 1956.6 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{100}H_{117}Br_4O_4S_8$: 1959.3425. Found: 1959.3488 [M$^+$+H].

4.1.5. 5,11,17,23-Tetrakis(terthienyl)-25,26,27,28-tetradecyloxycalix[4]arene Calix-OT(3). The coupling procedure described above was followed using **Calix-OT(2)-Br** (2 g, 1 mmol), 2-bromothiophene (3.26 g, 20 mmol), Mg turnings (3.9 g, 0.16 mmol), and $PdCl_2$(dppf) (16 mg, 2 mmol %) affording a dark yellow solid (1.54 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.26 (d, J=8 Hz, 4H), 7.15 (d, J=4.8 Hz, 4H), 7.05–7.04 (m, 20H), 6.85 (s, 4H), 6.76 (s, 4H), 4.49 (d, J=13.2 Hz, 4H), 3.94 (t, J=6.8 Hz, 8H), 3.23 (d, J=13.2 Hz, 4H), 1.95 (s, 8H), 1.41–1.29 (m, 56H), 0.9 (t, J=6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.5, 143.5, 137.3, 136.6, 135.5, 135.3, 135.1, 128.2, 127.8, 125.6, 124.4, 124.2, 124.0, 123.6, 123.4, 122.6, 75.5, 32.0, 31.1, 30.3, 30.0, 29.9, 29.8, 29.5, 26.4, 22.7, 14.1. MS (FAB) *m/z* 1969.7 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{116}H_{128}O_4S_{12}$: 1970.6484. Found: 1970.6421 [M$^+$].

4.1.6. 5,11,17,23-Tetrakis(5″-bromoterthienyl)-25,26,27,28-tetradecyloxycalix[4]arene Calix-OT(3)-Br. The bromination procedure described above was followed using **Calix-OT(3)** (0.61 g, 0.3 mmol) and NBS (0.2 g, 1.2 mmol) affording a dark yellow solid (0.66 g, 96% yield). ^{1}H NMR (270 MHz, $CDCl_3$, δ) 6.93 (s, 8H), 6.87–6.80 (m, 16H), 6.73 (d, J=5.4 Hz, 8H), 4.47 (d, J=13.2 Hz, 4H), 3.92 (t, J=5.4 Hz, 8H), 3.21 (d, J=13.2 Hz, 4H), 1.94 (s, 8H), 1.39–1.28 (m, 56H), 0.87 (t, J=5.4 Hz, 12H). ^{13}C NMR (67.5 MHz, $CDCl_3$, δ) 156.4, 143.6, 138.6, 136.9, 135.2, 134.8, 134.2, 130.5, 128.0, 125.6, 124.4, 124.2, 123.4, 123.1, 122.5, 110.6, 75.4, 32.1, 31.1, 30.4, 30.09, 30.07, 29.9, 29.5, 26.5, 22.8, 14.2. HRMS (MALDI-TOF) Calcd for $C_{116}H_{124}Br_4O_4S_{12}$: 2286.2859. Found: 2286.2850 [M$^+$].

4.1.7. 5,11,17,23-Tetrakis(quaterthienyl)-25,26,27,28-tetradecyloxycalix[4]arene Calix-OT(4). The coupling procedure described above was followed using **Calix-OT(3)-Br** (0.63 g, 0.28 mmol), 2-bromothiophene (0.9 g, 5.6 mmol), Mg (0.16 g, 6.7 mmol), and $PdCl_2$(dppf) (11 mg, 5 mmol %) to afford a dark yellow solid (0.4 g, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.17 (d, J=5.2 Hz, 8H), 7.06 (d, J=3.6 Hz, 8H), 6.96–6.86 (m, 20H), 6.79 (s, 8H), 4.49 (d, J=13.2 Hz, 8H), 3.94 (s, 8H), 3.23 (d, J=13.2 Hz, 8H), 1.96–1.94 (m, 8H), 1.41–1.25 (m, 56H), 0.89 (t, J=6.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.5, 143.6, 142.1, 136.55, 136.51, 136.4, 135.4, 135.2, 131.3, 128.7, 128.2, 125.7, 124.3, 124.2, 124.1, 123.7, 123.5, 122.6, 75.5, 32.0, 31.4, 30.4, 29.8, 29.5, 29.0, 28.6, 26.4, 22.7, 14.1. HRMS (MALDI-TOF) Calcd for $C_{132}H_{137}O_4S_{16}$: 2299.6073. Found: 2299.6157 [M$^+$+H]. Anal. Calcd for $C_{132}H_{136}O_4S_{16}$: C, 68.95; H, 5.96. Found: C, 69.14; H, 5.93.

Crystal data for **Calix-OT(2)**: $C_{72}H_{64}O_4S_8$, M_w=1249.71, crystal size=0.34×0.22×0.20 mm^3, monoclinic, space group *C2/c*, a=21.6040(14), b=22.1252(15), c=17.1240(11) Å, β=125.4460(10)°, V=6668.1(8) Å^3, Z=4, μ(Mo Kα)= 0.315 mm^{-1}. Intensity data were measured on a Bruker-AXS CCD area-detector diffractometer with graphite monochromated Mo Kα (λ=0.71073 Å) radiation, 15,702 reflections measured, 5670 unique, R(int)=0.0252. Final R=0.0594 and $wR2$=0.1568 for 3457 observed reflections with $I>2\sigma(I)$ and GOF=1.005.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication no. CCDC 606338. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.1.8. 1-Decyloxy-2,6-dimethyl-4-thienylbenzene M-OT(1). The coupling procedure described in the paper was followed using 1-decyloxy-2,6-dimethyl-4-bromobenzene (1 g, 2.9 mmol), 2-bromothiophene (2.5 g, 0.015 mol), Mg (0.45 g, 0.019 mol), and $PdCl_2$(dppf) (10 mg, 0.5 mmol %) affording a colorless liquid (0.88 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.22–7.20 (m, 2H), 7.03 (dd, J=4.8, 2.0 Hz, 1H), 3.76 (t, 2H), 2.30 (s, 6H), 1.84–1.77 (m, 2H), 1.52–1.48 (m, 2H), 1.38–1.28 (m, 12H), 0.89 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 155.8, 144.4, 131.4, 129.8, 127.8, 126.4, 124.1, 122.4, 72.5, 31.9, 30.4, 29.6, 29.57, 29.55, 29.3, 26.1, 22.7, 16.4, 14.1. MS (FAB) *m/z* 344.3 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{22}H_{32}OS$: 344.2173. Found: 344.2177.

4.1.9. 1-Decyloxy-2,6-dimethyl-4-(5-bromothienyl)benzene M-OT(1)-Br. The bromination procedure described in the paper was followed using **M-OT(1)** (1.17 g, 3.4 mmol) and NBS (0.6 g, 3.4 mmol) affording a blue sticky solid (1.4 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.15 (s, 2H), 6.98 (d, J=3.2 Hz, 1H), 6.93 (d, J=3.2 Hz, 1H), 3.75 (t, 2H), 2.30 (s, 6H), 1.82–1.78 (m, 2H), 1.51–1.48 (m, 2H), 1.33–1.28 (m, 12H), 0.88 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.2, 145.9, 131.6, 130.6, 129.0, 126.1, 122.5, 110.4, 72.5, 31.9, 30.4, 29.61, 29.57, 26.1, 22.7, 16.4, 14.1. MS (FAB) *m/z* 422.2 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{22}H_{31}BrOS$: 424.1255. Found: 424.1253 [M$^+$].

4.1.10. 1-Decyloxy-2,6-dimethyl-4-dithienylbenzene M-OT(2). The coupling procedure described in the paper was followed using **M-OT(1)-Br** (0.57 g, 1.34 mmol), 2-bromothiophene (1.1 g, 6.7 mmol), Mg (0.2 g, 8.3 mmol), and $PdCl_2$(dppf) (11 mg, 0.1 mmol %) affording a blue solid (0.53 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.24 (s, 2H), 7.20 (dd, J=4.2, 1.2 Hz, 1H), 7.17 (dd, J=4.2, 1.2 Hz, 1H), 7.12 (s, 2H), 7.02 (dd, J=4.8, 3.2 Hz, 1H), 3.77 (t, J=6.4 Hz, 2H), 2.31 (s, 6H), 1.83–1.77 (m, 2H), 1.52–1.48 (m, 2H), 1.38–1.24 (m, 12H), 0.89 (t, J=6.8 Hz, 3H). ^{13}C NMR (66 MHz, $CDCl_3$, δ) 155.8, 143.0, 137.5, 135.8, 131.4, 129.3, 127.7, 126.0, 124.4, 124.0, 123.2, 123.0, 72.5, 32.0, 30.5, 29.69, 29.66, 29.63, 29.4, 26.2, 22.8, 16.5, 14.2. MS (FAB) *m/z* 426.3 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{26}H_{34}OS_2$: 426.2051. Found: 426.2057.

4.1.11. 1-Decyloxy-2,6-dimethyl-4-($5'$-bromodithienyl)-benzene M-OT(2)-Br. The bromination procedure described in the paper was followed using **M-OT(2)** (0.53 g, 1.24 mmol) and NBS (0.22 g, 1.24 mmol) affording a yellow solid (0.6 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.23 (s, 2H), 7.09 (dd, J=3.6, 1.6 Hz, 1H), 7.03 (dd, J=4.0, 1.6 Hz, 1H), 6.96 (dd, J=3.6, 1.6 Hz, 1H), 6.90 (dd, J=3.6, 1.6 Hz, 1H), 3.76 (t, J=6.8 Hz, 2H), 2.30 (s, 6H), 1.82–1.79 (m, 2H), 1.52–1.48 (m, 2H), 1.33–1.28 (m, 12H), 0.89 (t, J=6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.1, 143.8, 139.1, 134.9, 131.6, 130.6, 129.2, 126.1, 124.8, 123.4, 123.0, 110.6, 72.5, 31.9, 30.4, 29.6, 29.58, 29.55, 29.3, 26.1, 22.7, 16.4, 14.1. MS (FAB) *m/z* 506.1 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{26}H_{33}BrOS_2$: 506.1132. Found: 506.1134 [M$^+$].

4.1.12. 1-Decyloxy-2,6-dimethyl-4-terthienylbenzene M-OT(3). The coupling procedure described in the paper was followed using **M-OT(2)-Br** (0.47 g, 0.93 mmol), 2-bromothiophene (0.76 g, 4.7 mmol), Mg (0.13 g, 5.6 mmol), and $PdCl_2$(dppf) (11 mg, 0.15 mmol %) affording a yellow solid (0.4 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.25 (s, 2H), 7.21 (dd, J=5.2, 1.2 Hz, 1H), 7.17 (dd, J=3.6, 1.2 Hz, 1H), 7.12 (dd, J=6.4, 4 Hz, 2H), 7.08 (dd, J=5.2, 3.6 Hz, 2H), 7.02 (dd, J=4.8, 3.6 Hz, 1H), 3.77 (t, J=6.4 Hz, 2H), 2.31 (s, 6H), 1.85–1.78 (m, 2H), 1.54–1.49 (m, 2H), 1.34–1.28 (m, 12H), 0.89 (t, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.1, 143.4, 137.2, 136.4, 135.9, 135.7, 131.6, 129.3, 127.9, 126.1, 124.47, 124.43, 124.4, 123.9, 123.6, 123.1, 72.6, 31.9, 30.4, 29.6, 29.57, 29.56, 29.3, 26.1, 22.7, 16.4, 14.1. MS (FAB) *m/z* 508.3 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{30}H_{36}OS_3$: 508.1928. Found: 508.1926.

4.1.13. 1-Decyloxy-2,6-dimethyl-4-($5''$-bromoterthienyl)-benzene M-OT(3)-Br. The bromination procedure described in the paper was followed using **M-OT(3)** (0.3 g, 0.6 mmol) and NBS (0.11 g, 0.6 mmol) affording a yellow solid (0.34 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.24 (s, 2H), 7.11 (dd, J=6.8, 4 Hz, 2H), 7.05 (d, J=3.6 Hz, 1H), 7.0 (d, J=4 Hz, 1H), 6.97 (d, J=3.6 Hz, 1H), 6.90 (d, J=3.6 Hz, 1H), 3.77 (t, J=6.8 Hz, 2H), 2.30 (s, 6H), 1.84–1.77 (m, 2H), 1.52–1.48 (m, 2H), 1.35–1.28 (m, 12H), 0.89 (t, J=6.8 Hz, 3H). ^{13}C NMR (66 MHz, $CDCl_3$, δ) 155.9, 143.4, 138.5, 136.8, 135.2, 134.6, 131.4, 130.5, 129.1, 125.9, 124.5, 124.4, 123.7, 123.4, 123.0, 110.8, 72.5, 32.0, 30.5, 29.70, 29.67, 29.63, 29.40, 26.2, 22.8, 16.5, 14.2. MS (FAB) *m/z* 588.2 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{30}H_{35}BrOS_3$: 588.1009. Found: 588.1005 [M$^+$].

4.1.14. 1-Decyloxy-2,6-dimethyl-4-quaterthienylbenzene M-OT(4). The coupling procedure described in the paper was followed using **M-OT(3)-Br** (0.4 g, 0.68 mmol), 2-bromothiophene (0.55 g, 3.37 mmol), Mg (0.1 g, 4.2 mmol), and $PdCl_2$(dppf) (11 mg, 2 mmol %) affording a yellow solid (0.34 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.25 (s, 2H), 7.22 (d, J=5.2 Hz, 1H), 7.18 (d, J=3.6 Hz, 1H), 7.12, (dd, J=6.0, 3.6 Hz, 2H), 7.08 (dd, J=5.2, 4 Hz, 2H), 7.02 (dd, J=4.8, 3.6 Hz, 1H), 3.77 (t, J=6.4 Hz, 2H), 2.37 (s, 6H), 1.83–1.79 (m, 2H), 1.52–1.48 (m, 2H), 1.34–1.28 (m, 12H), 0.89 (t, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 156.1, 143.5, 137.1, 136.6, 136.3, 135.9, 135.6, 131.6, 129.3, 127.9, 126.1, 124.5, 124.4, 124.3, 124.2, 123.9, 123.7, 123.2, 72.5, 31.9, 30.4, 29.6, 29.59, 29.56, 29.3, 26.2, 22.7, 16.4, 14.1. MS (FAB) *m/z* 590.3 [M$^+$]. HRMS (MALDI-TOF) Calcd for $C_{34}H_{38}OS_4$: 590.1805. Found: 590.1829.

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