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Novel Triindolo-Truxene Derivatives: Design, Synthesis, and Fine-Tuning of Electronic Properties and Molecular Assembly through Molecular Engineering

Jun-Bo Chen, Cen Zhou, Ru-Qiang Lu, Xin-Chang Wang, Hang Qu, Mithu Saha, Hao-Liang Liu, Hui Zhang and Xiao-Yu Cao* [a]

Abstract: Truxene-truxene, a C2-symmetric molecule with a large π-conjugated plane, has six methylene carbon atoms and three aromatic carbon atoms which can be facilely functionalized. Herein, we introduce butyl, carbonyl, cyano, and/or malononitrile groups into three methylene carbon atoms (6-, 14-, 22-, or 8-, 16-, 24-positions) and/or three aromatic carbon atoms (2-, 10-, and 18-positions) of triindolo-truxene to produce eight derivatives. Their photophysical and electrochemical properties, and molecular assembly can be effectively modulated by substituents and substitution patterns. Incorporation of electron-deficient groups led to red shifts in both the absorption and the emission of these derivatives, and also lowered their HOMO and LUMO levels. Different substitution patterns resulted in the different intramolecular donor-acceptor interactions. The substitutions of electron-deficient groups at 6-, 14-, and 22-methylene carbon atoms led to the intramolecular charge transfer from the fluorene arms to the truxene core, whereas the corresponding substitutions at 8-, 16-, and 24-methylene carbon atoms resulted in the converse intramolecular charge transfer from the truxene core to the fluorene arms. Their molecular packing in single crystals and molecular aggregation in solutions are also manipulated by their substituents and substitution patterns. This work provides a straightforward strategy to alter the properties of triindolo-truxene.

Introduction

Carbon-rich π-conjugated materials play key roles in organic electronics, such as organic field-effect transistors,[14] organic solar cells,[5-10] and organic light-emitting diodes.[11-15] To achieve high-performance organic devices, it is essential to develop new building blocks and to understand their structure–property relationships. In the past decades, several high-performance building blocks have been developed such as perylenediimide,[16-18] diketopyrrolopyrrole,[7,19-20] isoindigo,[21-23] and BDPy.[24-26] To alter their electronic properties, various substituents, such as alkyl groups, fluorene atoms, and cyano groups, have been introduced to their molecular backbones.[24,27]

Truxene, a well-performed and widely used building block in light-emitting[28-32] and hole-transporting[32-38] materials, features its adjustable properties through facile functionalizations.[39-40] Truxene possesses six aromatic carbon atoms in 2-, 3-, 7-, 8-, 12-, and 13-positions provided by three fluorene subunits (Figure 1), which can be functionalized by bromination,[41] acetylation,[42] nitration,[43] etc. In addition, the other three methylene carbon atoms in 5-, 10-, and 15-positions can also be substituted by alkyl groups,[49] carbonyl groups[42] or malononitrile groups.[45] Nonetheless, in most cases, these methylene carbon atoms can only be substituted by one type of functional groups that are usually alkyl chains to improve the solubility of truxene, thus limiting control over the properties of truxene. Triindolo-truxene, a favoured alternative structure synthesized by Pei et al.,[46] maintains the main structure of truxene while contains two sets of methylene carbon atoms (Figure 1). One set of methylene carbon atoms is in 6-, 14-, and 22-positions, and the other is in 8-, 16-, and 24-positions. These two sets of methylene carbon atoms can be substituted independently, providing more diverse combinations of substituents. However, the previous synthetic procedures, in which precursors undergo trimerization to form triindolo-truxene alkylated in 8-, 16-, and 24-positions, can hardly produce triindolo-truxene alkylated in 6-, 14-, and 22-positions. In addition, the effects of substituents and substitution patterns on triindolo-truxene have never been investigated.

Herein, we report new design and synthesis of eight triindolo-truxene derivatives (Figure 2), and the systematic investigation of their structure-property relationships. These eight triindolo-truxene derivatives were developed by introducing different substituents into three aromatic carbon atoms (2-, 10-, and 18-positions) and/or six methylene carbon atoms (6-, 14-, 22-, or 8-, 16-, 24-positions), including butyl, carbonyl, cyano, and malononitrile groups. The photophysical and electrochemical

![Figure 1. Molecular structures of truxene and triindolo-truxene.](image_url)

[a] J.-B. Chen, Dr. C. Zhou, R.-Q. Lu, Dr. X.-C. Wang, H. Qu, Dr. M. Saha, H.-L. Liu, Prof. H. Zhang, Prof. X.-Y. Cao
State Key Laboratory of Physical Chemistry of Solid Surfaces
Key Laboratory of Chemical Biology of Fujian Province
Collaborative Innovation Center of Chemistry for Energy Materials (ICChEM)
College of Chemistry and Chemical Engineering, Xiamen University
Xiamen 361005 (P. R. China).
Email: xcao@xmu.edu.cn

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measurements suggested that incorporating electron-deficient groups into trindolo-truxene can dramatically lower its energy levels and narrow its energy gap. In addition, the substitutions of electron-deficient groups at 6-, 14-, and 22-methylene carbon atoms led to different properties of trindolo-truxene compared with their analogues substituted at 8-, 16-, and 24-methylene carbon atoms. These influences of substituents and substitution patterns on the optical and electrochemical properties of trindolo-truxene derivatives were rationalized by density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. Moreover, their photoluminescence quantum yields and lifetimes can also be modulated by substituents and substitution patterns. We also investigated the molecular packing of these trindolo-truxene derivatives in single crystals through single crystal X-ray diffraction, as well as their aggregation in solutions via concentration-dependent \(^1\)H NMR. Our work provides efficient methods to construct trindolo-truxene and to manipulate its properties, which may facilitate its applications, for instance, in organic electronics and supramolecular chemistry.

**Results and Discussion**

**Synthesis of trindolo-truxene derivatives**

The synthetic approaches toward 2a–2d and 3a–3d are outlined in Scheme 1 and Scheme 2, respectively. Compound 6 was synthesized according to the similar method reported by Pei from 2-bromofluorene (see Supporting Information). Trimerization of compound 6 using POCl₃ as solvent gave 2a in 88% yield. The oxidation of 2a at 6-, 14-, and 22-methylene carbon atoms by oxygen in the presence of triton B and pyridine afforded 2b in 65% yield. Compound 2b was further treated by malononitrile to give 2d in 47% yield. Bromination of 2a at 2-, 10-, and 18-atoms produced compound 7. Then compound 7 was oxidized into compound 8 by oxygen in the presence of triton B. Compound 2c was obtained by cyanation of compound 8 in the total yield of 54%.

Friedel-Crafts acylation of 5,5,10,10,15,15-hexabutyltruxene afforded 11 in 83% yield. Compound 11 underwent Pd-catalyzed three-fold intramolecular couplings to give 3b in 59% yield. Compound 3d was obtained in 65% yield by treating 3b with malononitrile. Reduction of 3b using triethylsilane afforded 3a in 88% yield. Compound 3a was treated by bromide to give 12 in 88% yield. Oxidation of 12 using oxygen delivered 13 in 62% yield. The subsequent cyanation of 13 by copper(II) cyanide gave 3c in 94% yield. Notably, we have successfully developed a new
strategy to produce 6-, 14-, and 22-positions alkylation of triindolo-
truxene starting from 2a. The synthesis of 3a–3d was initiated from
5,5,10,11,15,16-hexabutytruxene. The truxene 3a, which is a full
complement of the previous synthetic route to produce 8-, 16-, and 24-positions alkylation triindolo-truxene 2a.

![Scheme 2. Synthetic approaches toward 3a–3d.](image)

**Photophysical properties**

The absorption spectra of eight derivatives in dichloromethane are illustrated in Figure 3, and the corresponding data are summarized in Table 1. As shown in Figure 3a and 3b, incorporating increasingly electron-deficient substituents into triindolo-truxene resulted in gradual red shifts of absorption onsets and absorption maxima in both series of 2a–2d and 3a–3d. The colors of the solutions changed from pale yellow (2a or 3a) to red (2d or 3d) (Figure 4). The absorption maximum of 2a is at 338 nm, whereas the absorption maxima of 2b–2d with increasingly electron-deficient substituents were red-shifted from 348 nm of 2b to 412 nm of 2d. In addition, the absorption onsets of 2a–2d were also red-shifted from 355 nm of 2a to 610 nm of 2d. The influences of substituents on absorption of 3a–3d are similar to those of 2a–2d (Table 1).

Moreover, substitution patterns also affect the photophysical properties of triindolo-truxene derivatives. A triindolo-truxene molecule contains two types of methylene carbons atoms. One type is in 6-, 14-, 22-positions, and the other is in 8-, 16-, 24-positions (Figure 1). Electron-deficient substituents at different types of methylene carbon atoms result in different absorption of corresponding triindolo-truxene derivatives (Figure S1). For example, compound 2b has carbonyl groups in 6-, 14-, 22-positions and butyl groups in 8-, 16-, and 24-positions, whereas 3b has butyl groups in 6-, 14-, 22-positions and carbonyl groups in 8-, 16-, and 24-positions (Figure 2). These different substitution patterns lead to much different absorption of 2b and 3b. Compound 2b shows three absorption peaks at 284 nm, 348 nm, and 368 nm, whereas 3b exhibits four absorption peaks at 263 nm, 307 nm, 361 nm, and 410 nm. To elucidate this difference, TD-DFT calculations were performed at the B3LYP/6-31G+(d) level of theory, and their natural transition orbitals (NTOs) corresponding to S0→S1 are shown in Figure S3–S10. The hole-NTOs of 2b–2d are localized on the truxene core while the electron-NTOs are delocalized over the whole molecule. Such distribution of NTOs indicates that the intramolecular charge transfer is from the truxene arms to the fluorene core. On the contrary, the hole-NTOs of 3b–3d are localized on the fluorene arms while the electron-NTOs are delocalized over the whole molecule, suggesting that the intramolecular charge transfer is from the...
truxene core to the fluorene arms. Thus, by changing the positions of substituents, we successfully developed different intramolecular donor-acceptor systems.

We also investigated the influences of substituents on the fluorescence of eight derivatives (Figure 3c and 3d). Increasing the electron deficiency of substituents led to progressively red-shifted emissions. The luminescent colors upon UV irradiation at 365 nm changed from pale yellow (2a or 3a) to red (2d or 3d), the emission maxima of 2a–2d are significantly red-shifted from 351 nm of 2a, which does not contain any electron-deficient substituents, to 602 nm of 2d, which has the strongest electron-deficient substituents. Compounds 3a–3d show similar tendency of fluorescence changes compared with that of 2a–2d. The photoluminescence quantum yields and lifetimes of eight triindolo-truxene derivatives were measured in dichloromethane (Table 1). Compound 2a shows a photoluminescence quantum yield of 32.27%, while 2b–2d exhibit much lower quantum yields aligned from 3.85% to 0.13% with the increasingly electron-deficient substituents. Compounds 3a, 3b, and 3c show quantum yields of 26.37%, 21.44%, and 29.17%, respectively. The strongly electron-deficient 3d exhibits a quantum yield of 0.38%. The lifetimes of 2a–2d are aligned from 2.34 ns to 0.82 ns, while the lifetimes of 3a–3d are in a range of 16.35 ns to 0.76 ns. These results indicate that different substituents and substitution patterns can modulate the photophysical properties of triindolo-truxene derivatives.

**Electrochemical properties**

To investigate the electrochemical properties of eight triindolo-truxene derivatives, cyclic voltammetry (CV) studies were employed in dichloromethane using a glassy carbon electrode as a working electrode, tetra-n-butylammonium hexafluorophosphate as electrolyte, and Fc/Fc⁺ as an external standard. The cyclic voltammograms are shown in Figure 5, and the corresponding data are summarized in Table 1. Increasing the electron deficiency of triindolo-truxene derivatives can progressively lower their HOMO and LUMO levels. The first oxidation potential onsets of 2a–2d were shifted from 1.17 V of 2a to 1.69 V of 2c. Thus, the HOMO levels of 2a–2d are aligned from −5.57 eV to −6.09 eV. The first reduction potential onsets of 2a–2d were shifted gradually from lower than −2 V of 2a to −0.37 V of 2d. Accordingly, the LUMO levels of 2a–2d are aligned from −2.03 eV of 2a (calculated from E₁/₂CV + EₚCV) to −4.03 eV of 2d. For 3a–3d, the changes of HOMO/LUMO levels are similar to those of 2a–2d. This efficient strategy to tune energy levels of triindolo-truxene can be used to design triindolo-truxene-based materials with different charge transport polarities (i.e., n-, p-channel or ambipolar transport). For instance, 2d exhibits the LUMO level as low as −4.03 eV. Such low LUMO level is beneficial for electron injection, hence making 2d a promising candidate for n-channel semiconductors.

In addition, the HOMO–LUMO band gaps of these derivatives were narrowed by introducing increasingly electron-deficient substituents. The band gaps are aligned from 3.49 eV of 2a to 2.04 eV of 2d, and from 3.49 eV of 3a to 2.35 eV of 3d. The shrinkage of band gaps is consistent with the red-shift of absorption. To further reveal the changes of HOMO/LUMO levels, DFT calculations were carried out at the B3LYP/6-311g(d,p) level of theory (Figure 6). The theoretical LUMO levels are aligned from −1.02 eV of 2a to −3.76 eV of 2d with increasing electron deficiency of the substituents, while the

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**Table 1. Summary of photophysical and electrochemical characterization of 2a–2d and 3a–3d.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax,abs, nm</th>
<th>λmax,em, nm</th>
<th>φF [%]</th>
<th>tΦ outlook, ns</th>
<th>E₁/₂CV, [V]</th>
<th>Eox,LUMO, [eV]</th>
<th>EₚCV, [eV]</th>
<th>Elumo, [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>355, 338</td>
<td>351, 367</td>
<td>32.27</td>
<td>1.84</td>
<td>−2.08</td>
<td>−5.57</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>500, 348</td>
<td>506, 527</td>
<td>3.85</td>
<td>2.34</td>
<td>−0.92</td>
<td>−3.48</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>492, 366</td>
<td>495, 520</td>
<td>1.52</td>
<td>1.85</td>
<td>−0.81</td>
<td>−3.59</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>610, 412</td>
<td>602</td>
<td>0.13</td>
<td>0.82</td>
<td>−0.37</td>
<td>−4.03</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>355, 340</td>
<td>362, 379</td>
<td>26.37</td>
<td>10.65</td>
<td>−2.18</td>
<td>−5.67</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>492, 410</td>
<td>512</td>
<td>21.44</td>
<td>13.57</td>
<td>−1.18</td>
<td>−3.22</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>490, 413</td>
<td>511</td>
<td>29.17</td>
<td>16.35</td>
<td>−0.97</td>
<td>−3.43</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>607, 498</td>
<td>601</td>
<td>0.38</td>
<td>0.76</td>
<td>−0.63</td>
<td>−3.77</td>
<td>2.35</td>
<td></td>
</tr>
</tbody>
</table>

[a] Measured in CH₂Cl₂ at room temperature. [b] Measured in CH₂Cl₂ with tetra-n-butylammonium hexafluorophosphate as electrolyte. [c] Determined against the external standard for Fc/Fc⁺. [d] EₚCV = Eₓ,LUMO – EᵪCV. [e] Calculated from the onsets of UV–vis absorption. [f] Shoulder peaks. [g] Not detected owing to that the reduction potential are out of the electrochemical window of CH₂Cl₂. [h] Eₓ,LUMO = EᵪCV + EₚCV.
HOMO levels are aligned from \(-5.51\) eV of 2a to \(-6.71\) eV of 2c. This result is in accordance with the tendency from experiments. The substitution patterns of electron-deficient groups also dramatically affect the LUMO levels of these derivatives. For example, compound 2b, whose carbonyl groups are in the 6-, 14-, and 22-positions, possesses a lower LUMO level than that of 3b, whose carbonyl groups are in the 8-, 16-, and 24-positions. Similar phenomena were also observed in other derivatives, which would be a consequence of different electronic structures. The LUMO of 2b is localized in the truxene core, while the LUMO of 3b most situates in its fluorene arms. This result reveals that different electronic structures were produced by introducing substituents into different types of methylene carbon atoms.\(^{[55-56]}\)

**Molecular assembly**

To reveal the effects of substituents and substitution patterns on molecular packing of triindolo-truxene derivatives, single crystals of these derivatives were obtained by phase-transfer or vapour-diffusion methods, and analysed by single crystal X-ray diffraction. The structures and molecular packing of 2c, 3a, 3c, and 3d are shown in Figure 7. Compound 2c displays an approximately planar molecular backbone. Its \(\text{C}_2\cdots\text{O}\) distances are about 3.0 Å, which indicate that three intramolecular hydrogen bonds are formed because these \(\text{C}_2\cdots\text{O}\) distances are shorter than those of the combined van der Waals radius (3.3 Å).
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Å.[57–58] These intramolecular hydrogen bonds are beneficial to the planarity of molecular backbone and then to its intermolecular packing. Four molecules of 2c form a stacked tetramer along the c axis with strong π−π interaction (π−π distance was ca. 3.4 Å). Their intermolecular π−π overlaps most focus on the center of molecule. These tetramers are organized in a layer-by-layer fashion with a 7.3 Å of interlayer distance. On the contrary, 3a, 3c, and 3d are difficult to stack along the cores of molecules owing to the large steric hindrance of butyl chains at 6-, 14-, and 22-positions. Compounds 3a and 3c arrange at edge-to-face modes, and both adopted herringbone stacking mode.[24] Compound 3d displays a layered packing mode with a π−π distance of 3.6 Å.

To investigate the aggregation of eight triindolo-truxene derivatives in solutions, concentration-dependent 1H NMR experiments of eight triindolo-truxene derivatives were performed in benzene-d6. Compound 2a showed a broadened 1H NMR spectrum at 298 K, which became sharper at elevated temperature (e.g. 333 K). At 333 K, the aromatic proton H4 of 2a was remarkably upfield shifted by 193 ppm when the concentration was increased from 0.1378 mM to 4.411 mM (Figure S17), suggesting an aggregation process. The self-association constant of 2a was determined to be 316 M−1 by an isodesmic aggregation model (Figure S18) at 333 K.[59] Compounds 2b and 2c also showed clear aggregation with self-association constants of 15 M−1 and 57 M−1 at 298 K, respectively (Figure S19–S22). In contrast, 2d and 3a–3d did not exhibit obvious changes of chemical shifts in aromatic region under various concentrations at 298 K (Figure S23–S27), probably due to that the bulky groups in 6-, 14-, and 22-positions of trindolo-truxene prohibit the molecular aggregation. These results confirm that substituents and substitution patterns can effectively alter molecular assembly of trindolo-truxene derivatives.

**Conclusions**

In summary, we have designed and synthesized eight trindolo-truxene derivatives with different combinations of butyl, carboxyl, cyano, or malononitrile substituents at six methylene carbon atoms (6-, 14-, 22-, or 8-, 16-, and 24-positions) and/or three aromatic carbon atoms (2-, 10-, and 18-positions) of trindolo-truxene. Their photophysical and electrochemical properties, as well as molecular packing in single crystals and aggregation in solutions can be finely tuned by different substituents and substitution patterns. The HOMO/LUMO levels of these trindolo-truxene derivatives are aligned from −5.57 eV/−2.08 eV to −6.13 eV/−4.03 eV, and their optical band gaps are ranged from 3.49 eV to 2.03 eV. We provide here not only the strategies of functionalizations on trindolo-truxene but also the systematic investigations on their structure-property relationships. The facile modifications, the tunable energy levels, and the controllable molecular packing of trindolo-truxene derivatives make them promising building blocks for organic electronics and also for constructions of more complicated architectures, such as covalent/metal organic frameworks,[60–61] molecular cages,[62] and supramolecular complexes.[63]

**Experimental Section**

**General remarks**

All of chemicals and solvents from commercial sources were utilized as received without further purification unless otherwise mentioned. 1H and 13C NMR spectra were recorded on a Bruker Avance II 400 MHz, Avance III 500 MHz, or Avance III 600 MHz NMR spectrometer. High-resolution mass spectra (HRMS) were recorded on Bruker En Apex Ultra 7.0T FTMS mass spectrometer or Bruker Impact II mass spectrometer. Absorption spectra were recorded on SHIMADZU UV-2550 spectrometer. Fluorescence measurements were recorded on HITACHI F-7000 fluorescence spectrophotometer. Photoluminescence quantum yields and lifetimes were recorded on Edinburgh FLs980 fluorescence spectrometer. Cyclic voltammetry (CV) was performed on a CHI660E electrochemical workstation in anhydrous dichloromethane containing n-Bu4NPF6 (0.1 M) as supporting electrolyte. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was 100 mV/s. Single crystal X-ray diffraction data were collected on Rigaku SuperNova X-Ray single crystal diffractometer using Cu Kα (λ = 1.54184 Å) micro-focus X-ray sources.

**Exemplified synthesis**

**Synthesis of 3b.** Compound 11 (0.20 g, 0.146 mmol), KOAc (0.12 g, 1.17 mmol), tetrabutylammonium bromide (0.24 g, 0.73 mmol), Pd(OAc)2 (0.013 g, 0.058 mmol), and anhydrous N,N-dimethylformamide (3 mL) were added in a Schlenk tube. After removing oxygen by three freeze-pump-thaw cycles, the reaction was heated at 153 °C for 36 h. The solution was cooled and poured into ice water. The precipitate was filtered, and dissolved using dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous sodium sulphate. The crude product was purified by column chromatography over silica gel using a mix solvent of petroleum ether and dichloromethane (1:1, v/v) as mobile phase to afford 3b as a yellow solid (0.084 g, 59%). 1H NMR (500 MHz, CDC13, 298 K) δ (ppm) = 8.56 (s, 3H), 7.83 (s, 3H), 7.73 (t, J = 7.0 Hz, 6H), 7.61 (t, J = 6.0 Hz, 3H), 7.36 (t, J = 7.0 Hz, 3H), 2.97–2.94 (m, 6H), 2.30–2.26 (m, 6H), 0.99–0.92 (m, 12H), 0.68–0.67 (m, 6H), 0.56–0.54 (m, 6H), 0.49 (t, J = 7.3 Hz, 18H). 13C NMR (126 MHz, CDC13, 298 K) δ (ppm) = 193.83, 155.09, 149.46, 145.64, 144.72, 143.60, 138.10, 135.12, 134.90, 133.25, 129.07, 124.38, 119.90, 118.37, 116.31, 55.93, 36.81, 26.68, 22.80, 13.79. APCH-IRMS (m/z): [M+H]+ calc. for C38H24N2O2S: 583.5554; found, 583.5553.

**Synthesis of 3a.** Compound 3b (5.2 g, 5.3 mmol) was dissolved in anhydrous dichloromethane (38 mL). Under a nitrogen atmosphere, Et3SiH (12.3 g, 106 mmol) was added, and the solution was stirred for 10 min. Then BF3·OEt2 (15.0 g, 106 mmol) was slowly added. The solution was warmed to room temperature and stirred at room temperature for 24 h until becoming colourless. The reaction was quenched by saturated sodium carbonate solution. The organic layer was washed with water and brine, and dried over anhydrous sodium sulphate. The crude product was purified by column chromatography over silica gel with petroleum ether as mobile phase to afford 3a as a white solid (4.4 g, 88%). 1H NMR (500 MHz, CDC13, 298 K) δ (ppm) = 8.86 (s, 3H), 7.99 (d, J = 7.5 Hz, 3H), 7.68 (s, 3H), 7.62 (d, J = 7.0 Hz, 3H), 7.49 (t, J = 7.5 Hz, 3H), 7.35 (t, J = 7.0 Hz, 4.06 (s, 6H), 3.19–3.15 (m, 6H), 2.30–2.26 (m, 6H), 0.98–0.91 (m, 12H), 0.70–0.63 (m, 12H), 0.44–0.47 (m, 18H). 13C NMR (126 MHz, CDC13, 298 K) δ (ppm) = 153.74, 144.88, 143.57, 142.45, 142.08, 140.13, 139.30, 138.54, 126.82, 126.38, 125.20, 119.32, 118.90, 115.83, 55.29, 36.96, 36.86, 26.76, 22.97, 13.90. APCH-IRMS (m/z): [M+H]+ calc. for C37H28Si: 543.6176; found, 543.6200.

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