Insights into the triple self-condensation reaction of thiophene-based methyl ketones and related compounds

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Abstract

The acid catalysed triple self-condensation of 1-thien-2-ylethanone (2-acetylthiophene) and five related compounds is presented. Tetrachlorosilane used as the Lewis acid produces dry hydrogen chloride which catalyzes the self-condensation process. Depending on the reaction conditions and the substitution of the carbonyl substrates, the reaction can proceed as a [2+2+2] cyclotrimerization towards C3-symmetric 1,3,5-trisubstituted benzenes, or as the single-type aldol condensation leading to 1,3-disubstituted (E)-β-methylchalcones. This is important for the design of new aromatic/olefinic compounds beyond the model structures. Synthesis of 4'-fluoro-3,5-di-(2-thienyl)biphenyl through a mixed-type aldol reaction using erbium triflate is discussed. Mechanistic rationale is provided.

Keywords: [2+2+2] Cyclotrimerization, aldol condensation, 1,3,5-trisubstituted benzene, β-methylchalcone
Introduction

Star-shaped molecules based on 1,3,5-triarylbenzenes have long been recognized as a family of amorphous glasses stable above room temperature. The bioisosteric replacement of benzene by thiophene has extended the family of \( C_3 \)-symmetric compounds and their applications in electroluminescent (EL) devices, liquid crystalline materials and as fluorescent probes. In contrast to polymers used in similar applications, amorphous molecular materials are pure materials with well-defined molecular structures and definite molecular weights without any distribution. Consequently, 1,3,5-tri(het)arylbenzenes serve as versatile platforms in the design of organic light emitting diodes (OLEDs), dendrimers, polycyclic aromatic hydrocarbons (PAH), bulky ligands and truxenes (derivatives of 10,15-dihydro-5\( H \)-diindeno[1,2-\( a \); 1',2'-c]fluorene). The classical one-directional convergent synthetic approach, originally developed by Clapps and Morton, is that most frequently reported in the literature.

The \([2+2+2]\) cyclotrimerization of acetophenones and related compounds is expected to have outstanding potential because of its high atom economy and broad reaction scope. The triple self-condensation of starting acetophenones (AP) and hetaryl methyl ketones (HetAP) takes place mostly in ethanol using Brønsted or Lewis acids such as common \( \text{SiCl}_4 \), \( \text{TiCl}_4 \), \( p\)-TsOH and variations on more complex structures. Although these processes provide regioselective approaches to polysubstituted aromatic compounds, as has been presented in a large number of studies, there are some limitations including low yields, long reaction times, harsh reaction conditions, use of expensive metal catalysts, tedious work-up, and formation of side products.

It is generally known that \([2+2+2]\) cyclotrimerization involving bulky substrates is not a trivial task. The presence of a bulky substituent in the structure of the starting ketone can change the reactivity in favour of formation of appropriate \((E)\)-\( \beta \)-methylchalcones (dypnones), derivatives of \((E)\)-1,3-diphenyl-2-buten-1-one. This is because the triple self-condensation of acetophenones (AP) or hetaryl methyl ketones (HetAP), respectively, under mild reaction conditions (ambient temperature, efficient catalysis) occurs as a stepwise process, as was independently highlighted by Wu et al. and Wagh and Akamanchi. The acid catalyzed single-type aldol condensation of two equivalents of starting carbonyl compounds AP or HetAP towards the formation of \((E)\)-\( \beta \)-methylchalcones (BMC) occurs first, followed by subsequent enolization and rearrangement of BMC into final 1,3,5-triarylbenzenes (TAB) or 1,3,5-trihetarylbenzenes (THetAB). The bulky substitution as well as the electron-withdrawing substituents in the structure of acetophenones inhibit the second aldol reaction affording only the corresponding \((E)\)-\( \beta \)-methylchalcones. There are two possibilities of cyclization, \emph{i.e.} two equivalents of \((E)\)-\( \beta \)-methylchalcone reacts to create \( C_3 \)-symmetric benzenes (Scheme 1, A) or a molecule of the key intermediate dypnone undergo condensation with another molecule of the carbonyl substrate (Scheme 1, B).

\[ \begin{align*}
1a: X = & \text{H} \\
1b: X = & \text{Me} \\
1c: X = & \text{Cl} \\
1d: X = & \text{Br}
\end{align*} \]

\[ \begin{align*}
1e: X = & \text{H} \\
1f: X = & \text{H}
\end{align*} \]

\[ \begin{align*}
1g: X = & \text{Me} \\
1h: X = & \text{Cl}
\end{align*} \]

**Figure 1.** Structures of the starting carbonyl substrates under investigation.
The formation of (E)-β-methylchalcones/dypnones during the process of cyclotrimerization is indeed underrated. Besides which, dypnone-involved organic synthesis is important further i.e. in a mixed-type aldol condensation towards unsymmetrically branched 1,3,5-trisubstituted benzenes, in the reduction towards diols or in the synthesis of allicyclic azides. In this regard, we have studied the process of the triple self-condensation of hetaryl methyl ketones in the construction of either C3-symmetric 1,3,5-trihetaryl benzenes or 1,3-bishetaryl (E)-β-methylchalcones/dypnones, or the mixture of the two possible compounds. Thien-2-yl-ethanone 1a and its C5 methyl- and halogen-substituted derivatives 1b-d were selected for our investigations under the different experimental conditions (Figure 1), either affecting the triple self-condensation by tetrachlorosilane (SiCl4, 2-4 equiv.) combined with a solvent change (ethanol, ethanol/toluene mixture, 2-ethoxyethanol) or by use of trifluoromethanesulfonic acid as a Brønsted acid catalyst (TFSA-CF3SO3H, 2 mol %) in toluene. In fact, SiCl4 and related weak Lewis acids in anhydrous alcohols produce controlled amount of dry hydrogen chloride (g) acting as the acid catalyst in aldol-type condensations. Our study was extended employing 1-[5-(fluoren-9-ylidenemethyl)thien-2-yl]ethanone (1e) and 1-[5-(fluoren-9-ylidenemethyl)-1-methyl-1H-pyrrol-2-yl]ethanone (1f) with a bulky fluorenylidenemethyl substituent at the C5 position of the thiophene and pyrrole rings (Figure 1), to examine the effect of the substitution on the reaction. The synthesis of 1,3,5-unsymmetrically substituted benzene is presented according to a mixed-type aldol condensation of the appropriate (E)-β-methylchalcone and p-fluoroacetophenone.

Scheme 1. [2+2+2] Cyclotrimerization reaction of acetophenones and related compounds. Two possible routes to C3-symmetric benzene formation are highlighted.

Results and Discussion

Effects of solvent, temperature and reaction time
The [2+2+2] cyclotrimerization of starting ketones 1a-d was carried out at room temperature (25 °C). The same approach with ketones 1e and 1f was conducted at 100 °C. Generally, a relatively low temperature of the triple self-condensation towards 1,3,5-triarylbenzenes has to be maintained to form thermodynamically stable enol-silyl ether reactive intermediates of the excited state followed by in situ formation of gaseous HCl. Although in the triple self-condensation process promoted by SiCl4 as the weak Lewis acid, ethanol proves to be the most universal solvent (Method A), the solubility of some hetaryl methyl ketones 1a-f in ethanol might be insufficient. Since the enhanced solubility of substrates together with the activity of tetrachlorosilane was crucial, we performed the [2+2+2] cyclotrimerization with the starting substrates 1a-d in...
a mixture of ethanol/toluene (Method B)\textsuperscript{16,20} as well as by using 2-ethoxyethanol instead of ethanol (Method C). Use of a double and threefold excess of SiCl\textsubscript{4}/EtOH (Method A and B) leads directly to 1,3,5-triarylbenzenes 3a-d,\textsuperscript{3} while use of excess of catalyst (4 equiv.) in 2-ethoxyethanol (Method C) gave good yields of β-methylchalcones 2b-d.\textsuperscript{17,36} Since, fluorenylidene-substituted hetaryl methyl ketones 1e and 1f were insoluble in the solvents used according to Methods A-C, we turned to Method D, performing the reaction with trifluoromethane sulfonic acid (TFSA, 2 mol \%) in toluene. The optimal reaction time during which the formation of unidentifiable polymers was suppressed was 14 h with SiCl\textsubscript{4} (Methods A-C) and 30 h with CF\textsubscript{3}SO\textsubscript{3}H (Method D). The results on reaction conditions for 1a-f are summarized in Table 1.

Table 1. The reaction conditions of [2+2+2] cyclotrimerization of thiophene-based methyl ketones 1a-e and pyrrolyl substrate 1f

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction conditions</th>
<th>Solvent</th>
<th>Substrat</th>
<th>Product / Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method A</td>
<td>SiCl\textsubscript{4} (0.078 mol, 2 equiv.), 14 h, 25 °C</td>
<td>EtOH</td>
<td>1a</td>
<td>3a / TSC\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1c</td>
</tr>
<tr>
<td>Method B</td>
<td>SiCl\textsubscript{4} (0.117 mol, 3 equiv.), 14 h, 25 °C</td>
<td>EtOH/PhMe (50:50)</td>
<td>1a</td>
<td>2a / aldol condensation\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1d</td>
</tr>
<tr>
<td>Method C</td>
<td>SiCl\textsubscript{4} (0.156 mol, 4 equiv.), 14 h, 25 °C</td>
<td>2-Ethoxyethanol</td>
<td>1a</td>
<td>3a / TSC\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1d</td>
</tr>
<tr>
<td>Method D</td>
<td>CF\textsubscript{3}SO\textsubscript{3}H (0.1 mmol, 2 mol %)</td>
<td>PhMe</td>
<td>1e</td>
<td>2e / aldol condensation\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1f</td>
</tr>
</tbody>
</table>

\textsuperscript{a} TSC = triple self condensation of three equivalents of the starting substrates ([2+2+2] cyclotrimerization), according to results presented later in this research work; \textsuperscript{b} Aldol condensation – single-type of aldol condensation between two molecules of the starting ketones, according to results presented later in this research work; \textsuperscript{a, b} According to the mechanism discussed below.

Mechanism

To the best of our knowledge, two possible mechanisms of acid catalysed [2+2+2] cyclotrimerization of aryland hetaryl methyl ketones have been reported recently.\textsuperscript{36,37} In both approaches, the crucial intermediate, (E)-β-methylchalcone/dypnone, was initially formed via the single-type aldol condensation of two equivalents of acetophenones and related compounds activated by the acid catalyst (Scheme 2).\textsuperscript{34-36} Since (E)-β-methylchalcones/dypnones were stable compounds, in several cases they were isolated as the final products and the subsequent formation of 1,3,5-trisubstituted benzenes was not observed. The reactivity of (E)-β-methylchalcone/dypnone was crucial in the subsequent cyclization and aromatization reaction sequence, which may occur in the reaction with another amount of the starting carbonyl compound in the single-type aldol condensation (route A)\textsuperscript{34} subsequently followed by intramolecular rearrangement supporting the ring closure (Scheme 2). In the second approach (route B)\textsuperscript{35} the single-type aldol condensation occurs first between
two equivalents of the (E)-β-methylchalcone/dypnone, continuing as intramolecular [2+2] cycloaddition and subsequent retro [2+2] cycloaddition leading to 1,3,5-trisubstituted benzenes (Scheme 2). The bulky substituent may inhibit either the aldol condensation with another equivalent of the starting ketone (route A) or the aldol addition with another equivalent of the dypnone (route B). The dypnone’s ability to precipitate from the reaction mixture as well as the solubility of the carbonyl substrate influences the process of [2+2+2] cyclotrimerization to a large extent. Again, the use of SiCl₄ generates -OSiCl₃ protected hydroxyl compounds, allowing to stop the addition at the aldol step.

Scheme 2. Proposed mechanism of a triple self-condensation reaction sequence of 1-thien-2-ylethanone (1a). The H⁺ cation originates from dry HCl (g) which is generated in situ from SiCl₄ through the the excited state enolsilyl reactive intermediates.®ARKAT USA, Inc

Self condensation vs. [2+2+2] cyclotrimerization of starting carbonyl compounds 1a-f
With optimized reaction conditions and insight on the mechanism, the scope of the reaction towards the formation either C₃-symmetric 1,3,5-trisubstituted benzenes via [2+2+2] cyclotrimerization, or (E)-β-methylchalcones/dypnones by the single-type aldol condensation was investigated (Table 2).

The reaction of 1-thien-2-yl-ethanone (1a), 1-(5-methylthien-2-yl)ethanone (1b) and 1-(5-chlorothien-2-yl)ethanone (1c) performed under the standard conditions (Method A, SiCl₄/EtOH) affording the 1,3,5-trisubstituted benzenes: 1,3,5-tris(thien-2-yl)benzene (3a), 1,3,5-tris(5-methylthien-2-yl)benzene (3b) and 1,3,5-tris-(5-chlorothien-2-yl)benzene (3c), respectively, in yields not exceeding 60%. The [2+2+2] cyclotrimerization of bromo-substituted derivative 1d by Method B (SiCl₄, EtOH/PhMe) produced C₃-symmetric 1,3,5-trisubstituted benzene 3d in a moderate 28% yield, probably as a result of the side polymerization reactions characteristic for bromo-derivatives of thiophenes. By alternating the solvent with 2-ethoxyethanol (Method C) for 1a-1d only the reaction with 1a proceeded as [2+2+2] cyclotrimerization leading
to 1,3,5-tris(thien-2-yl)benzene (3a, 35%), while in the case of its methyl-, chloro- and bromo-substituted derivatives 1c-1d (E)-β-methylchalcones/dypnones 2b (33%), 2c (64%) and 2d (31%) were isolated as a consequence of the single-type aldol condensation. 1,3-Dithienyl-substituted (E)-β-methylchalcone 2a was finally isolated in the yield of 45% performing the reaction in EtOH/PhMe (50:50) mixture (Method B).

As expected, from the reactions carried out with the 1-(5-fluoren-9-ylidenemethyl)thien-2-yl)ethanone (1e) and the 1-(5-fluoren-9-ylidenemethyl-1-methyl-1H-pyrrol-2-yl)ethanone (1f), bearing the bulky fluorenylidene residues, in PhMe/TFSA (Method D) (E)-β-methylchalcones/dypnones 2e,f were isolated in yield of 33% in both cases (Table 2). Concerning the substitution, the reaction with 1e,f was completed as single-type aldol condensation without the formation of any C3-symmetric benzenes.

Table 2. Summary of triple self-condensation of heterocyclic methyl ketones 1a-f

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Conditions / Method / Process</th>
<th>Product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2</td>
<td>(1a)</td>
<td>(3a)</td>
<td>(\text{SiCl}_4) / EtOH / 2-ethoxyethanol / Method A / Method C / [2+2+2] cyclotrimerization</td>
<td>(55%) / (35%)</td>
</tr>
<tr>
<td>3</td>
<td>(1b)</td>
<td>(3b)</td>
<td>(\text{SiCl}_4) / EtOH / Method A / [2+2+2] cyclotrimerization</td>
<td>(58%)</td>
</tr>
<tr>
<td>4</td>
<td>(1c)</td>
<td>(3c)</td>
<td>(\text{SiCl}_4) / EtOH / Method A / [2+2+2] cyclotrimerization</td>
<td>(58%)</td>
</tr>
<tr>
<td>5</td>
<td>(1d)</td>
<td>(3d)</td>
<td>(\text{SiCl}_4) / EtOH/PhMe / Method B / [2+2+2] cyclotrimerization</td>
<td>(28%)</td>
</tr>
<tr>
<td>6</td>
<td>(1a)</td>
<td>(2a)</td>
<td>(\text{SiCl}_4) / EtOH/PhMe / Method B / Single-type aldol condensation</td>
<td>(45%)</td>
</tr>
<tr>
<td>7</td>
<td>(1b)</td>
<td>(2b)</td>
<td>(\text{SiCl}_4) / 2-ethoxyethanol / Method C / Single-type aldol condensation</td>
<td>(33%)</td>
</tr>
</tbody>
</table>
Table 2. Continued

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Conditions / Method / Process</th>
<th>Product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td><img src="image1" alt="" /></td>
<td><img src="image2" alt="" /></td>
<td>SiCl₄ / 2-ethoxyethanol Method C</td>
<td>2c (64%)</td>
</tr>
<tr>
<td>9</td>
<td><img src="image3" alt="" /></td>
<td><img src="image4" alt="" /></td>
<td>SiCl₄ / 2-ethoxyethanol Method C</td>
<td>2d (31%)</td>
</tr>
<tr>
<td>10</td>
<td><img src="image5" alt="" /></td>
<td><img src="image6" alt="" /></td>
<td>CF₃SO₃H / PhMe Method D</td>
<td>2e (33%)</td>
</tr>
<tr>
<td>11</td>
<td><img src="image7" alt="" /></td>
<td><img src="image8" alt="" /></td>
<td>CF₃SO₃H / PhMe Method D</td>
<td>2f (33%)</td>
</tr>
</tbody>
</table>

Effect of substitution

To examine effects of the substituent X we have compared the results of formation 1,3,5-triarylbenzene 3a-d and (E)-β-methylchalcones 2a-d from substrates 1a (X = H), 1b (X = Me), 1c (X = Cl) and 1d (X = Br) (Figure 1). Results showed that substrate 1c possessing chlorine provided best results in both [2+2+2] cyclotrimerization approach towards 1,3,5-trisubstituted benzene 3c as well as in a single-type aldol condensation leading to (E)-β-methylchalcone 2c (Entries 4 and 8, Table 2). On the other hand, both types of the reaction with bromo-substituted substrate 1d (Entries 5 and 9, Table 2) were less effective, probably due to the enhanced ability of brominated thiophenes to undergo polymerization. According to generally-accepted fact in comparison with obtained results, we can assume that electron-withdrawing effect of the halogen substituent in the α-position (C5) of the thiophene for substrates 1c and 1d (X = Cl, Br) induced the single-type aldol condensation more efficiently than the triple self-condensation process: (E)-β-methylchalcone 2c vs. 1,3,5-trisubstituted benzene 3c = 64% yield (Entry 8, Table 2) vs. 58% yield (Entry 4, Table 2); (E)-β-methylchalcone 2d vs. 1,3,5-trisubstituted benzene 3d = 29% yield (Entry 9, Table 2) vs. 31% (Entry 5, Table 2), respectively. The most significant effect of the substitution on the reaction proceeding was with substrates 1e and 1f possessing fluorenylidene residue. The steric hindrance inhibited the second aldol reaction towards formation of the benzene ring once appropriate (E)-β-methylchalcones 2e (33%, Entry 10, Table 2) and 2f (33%, Entry 11, Table 2) are formed. The thienyl methyl ketone without substitution (1a, X = H) or bearing methyl substituent (1b, X...
= Me) proceeded moderately in both, in [2+2+2] cyclotrimerization reaction (43% and 35% for 3a, Entry 1 and 2; 41% for 3b, Entry 3) and in a single-type aldol condensation (45% for 2a Entry 6; 33% for 2b, Entry 7, Table 2).

Taken together, we assumed that the self-condensation reactions of thiophene-based methyl ketones and related compounds were governed by several factors, such as electronic and steric effects of substituents at C5 position of the heterocyclic core together with reaction conditions (Methods A-D) applied for a particular substrate.

1,3,5-Symmetrically-substituted benzenes 3a-d appear in their $^1$H NMR spectra as singlets at 7.75–7.40 ppm due to aromatic hydrogen and in the range of 7.10–7.75 ppm as doublets or triplets of the thiophene core hydrogens. The H-α proton of the double bond for (E)-β-methylchalcones 2a-f resonate in the range of 6.85–7.10 ppm as singlets or quartets as the result of the field interaction between olefinic hydrogen and hydrogen on C-β position of the thiophene together with interactions with the neighbouring methyl group. The methyl group signals appeared at 2.50 ppm.

Mixed-type aldol condensation

The scope of dypnone-involved organic synthesis was expanded performing the reaction of 2a (2.0 equiv.) with $p$-fluoracetophenone (1.0 equiv.) as the aldol-type addition promoted by erbium triflate [Er(OTf)$_3$, 1.0 mol %].

The strong electron-withdrawing capacity of the methanesulfonate anion enhances the Lewis acid character of the catalyst and among the lanthanoid(III) triflates Er$^{3+}$ was one of the most active cations.

To the best of our knowledge, this is the first example of the dypnone-like aldol reaction catalysed by erbium triflate. Unsymmetricaly substituted 1,3,5-benzene 4 was isolated after heating at the boiling point of toluene (8 h, 62%, Scheme 3). In the $^1$H NMR spectrum only aromatic hydrogen signals appear in the range of 8.00–7.10 ppm indicating the full conversion of the starting (E)-β-methylchalcone 2a.

Scheme 3. Mixed-type aldol reaction of 2a forming an unsymmetrically branched 1,3,5-benzene 4 catalysed by erbium triflate.

Conclusions

In this study we have complemented and compared the known aspects of the [2+2+2] cyclotrimerization reactions of acetophenones and related compounds with our current results. The course of the self-condensation process is indeed challenging providing the possibility of formation of different type of compounds: the C$_3$-symmetric aromatic derivatives or the unsaturated (E)-β-methylchalcones (dypnones). We have highlighted, that by varying the substitution of carbonyl substrates in combination with different reaction conditions the reaction can be directed either in a triple [2+2+2] cyclotrimerization manner towards 1,3,5-tris(thien-2-yl)benzenes 3a-d (Table 2, Entries 1-5), or in accordance with a single-type aldol condensation producing 1,3-disubstituted (E)-β-methylchalcones 2a-f (Table 2, Entries 6-11). The ability to access new
compounds 2b-f through the general and simple protocols (Method B) or by their slight variations (Method C – use of ethyleneglycole monoethylether as solvent, Method D – use of trifluoromethane sulfonic acid as acid catalyst) is also described. The outlook of the synthetic application of (E)-β-methylchalcones yielding unsymmetrical 1,3,5-triarylbenzene derivatives is presented on the example of synthesis of (E)-3-(2,2′-dithienyl)-5-(fluorenyl)benzene (4). Both types of designed structures are important in a broad range of applications; 1,3,5-trisubstituted benzenes in the synthesis of star-shaped molecules acting as the π-conjugated units in opto-electronic materials and 1,3-disubstituted (E)-β-methylchalcones as intermediates in organic synthesis.

**Experimental Section**

**General.** All commercially available chemicals were used as received without further purification. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) on plates precoated with silica gel (Merck 60 F254) and visualized using a UV hand lamp operating at 254/365 nm wavelengths. Melting points were recorded on a Kofler block and are uncorrected. The infrared spectra were taken on Agilent Cary 630 FTIR spectrometer with diamond ATR. Elemental analyses (EA) were performed on a Flash EA 2000 CHNS/O-OEA analyser. ESI-MS spectrum of compound 4 containing fluorine in the structure was recorded on Mass Quattro LC. NMR spectra (1H at 300 and 13C at 75 MHz) were obtained on the Varian VXR-300 spectrometer and products were reported relative to tetramethylsilane (TMS, 0.00 ppm) or CDCl3 (7.24 ppm) or DMSO-d6 (2.49 ppm) for 1H NMR data, CDCl3 (77.0 ppm) or DMSO-d6 (39.7 ppm) for 13C NMR data. Spectral data are presented as follows: chemical shifts in part per million (ppm), coupling constants J (Hz) and splitting patterns as s = singlet, d = doublet, t = triplet, q = quadruplet, dd = doublet of doublets, m = multiplet. Absorption spectra of the solutions in chloroform (CHCl3), or dichloromethane (CH2Cl2) with concentration 1.10⁻⁵ mol·dm⁻³ measured on a UV 1650PC spectrometer (Shimadzu, Japan).

Thien-2-ylethanone (1a) and its C5 methyl-, chloro-, bromo- and fluorenylidene-substituted derivatives 1b-e were synthesized following the published procedures.⁴⁵-⁴⁷ 1-{5-[5H-Fluorene-9-ylidene)methyl]-1-methyl-1H-pyrrol-2-yl}ethanone (1f) was synthesized in two steps according to Scheme 4 following the acetylation procedure published by us previously.⁴⁸

![Scheme 4](image)

Scheme 4. Synthesis of fluorenylidene-substituted 2-acetyl-1H-methylpyrrole substrate 1f.

1-{5-[5H-Fluorene-9-ylidene)methyl]-1-methyl-1H-pyrrol-2-yl}ethanone (1f). To a solution of 1-methyl-1H-pyrrole-2-carbaldehyde (0.06 mol, 6.5 g) and fluorene (0.06 mol, 10.0 g) in toluene (40 mL) sodium hydroxide (1.4 mol, 56.0 g) in water (84 mL) was added. To the toluene/water mixture the phase transfer catalyst n-butyltetraammonium bromide (n-Bu₄NBr, 0.01 mol, 3.5 g) was added and the mixture was left to stir at room
temperature (25 °C) overnight (6-8 h). After the reaction was completed the mixture was extracted with toluene (3 × 20 mL). Combined organic layers were washed with 0.1 M HCl (20 mL), then with water (2 × 20 mL) and finally with saturated solution of NaCl (20 mL). The organic layer was dried (Na₂SO₄) and solvent evaporated under reduced pressure. Crude product was purified by flash column chromatography (eluent: n-hexanes/EtOAc, 90:10) to give the intermediate: 2-[(9H-fluorene-9-ylidene)-methyl]-1-methyl-1H-pyrrole (1f') as a yellow oil. Yield 73% (11.3 g). 1H NMR (300 MHz, CDCl₃) δ (ppm) 3.71 (s, 3H, N-CH₃); 6.36 – 6.32 (m, 1H, pyrrole); 6.80 – 6.76 (m, 2H, pyrrole); 7.24 – 7.22 (m, 1H, pyrrole); 7.37 – 7.32 (m, 4H, fluorenyl); 7.76 – 7.72 (m, 3H, fluorenyl); 8.23 (d, J = 7.8 Hz, 1H, fluorenyl). 13C NMR (75 MHz, CDCl₃) δ (ppm) 34.4, 108.5, 112.8, 115.8, 119.5, 119.6, 119.7, 123.7, 124.4, 126.7, 126.8, 127.6, 128.2, 129.0, 134.4, 136.6, 138.6, 139.7, 140.6. Anal. Calc. for C₁₉H₅N (257.33 g·mol⁻¹): C, 88.68; H, 5.88; N, 5.44. Found: C, 88.70; H, 6.04; N, 5.22%. λ_max (CHCl₃) = 250, 258, 391 nm.

The mixture of 2-[(9H-fluorene-9-ylidene)methyl]-1-methyl-1H-pyrrole (1f', 0.039 mol, 10.0 g) in acetic acid anhydride (acting as the solvent and as the acylating agent in the same time, 43.039 mol, 4.0 mL) with magnesium perchlorate dihydrate [Mg(ClO₄)₂·2H₂O, 0.01 equiv., 0.39 mmol, 42 mg] was left to stir at 80 °C for 6 h. After the reaction was completed (TLC monitoring) the mixture was poured to ice (30 mL) and then extracted with diethylether (3 × 30 mL). The solvent was evaporated under reduced pressure and crude product was purified by flash column chromatography (eluent: toluene) to give 1-{5-[(9H-fluorene-9-ylidene)methyl]-1-methyl-1H-pyrrol-2-yl}ethanone (1f) as pale yellow solid. Yield 45% (5.3 g), mp 150-152 °C. 1H NMR (300 MHz, CDCl₃) δ (ppm) 2.50 (s, 3H, COCH₃), 3.95 (s, 3H, NCH₃), 6.56 (d, J₄,₃ = 4.2 Hz, 1H, H-₄ pyrrole), 7.06 (d, J₃,₄ = 4.2 Hz, 1H, H-₃ pyrrole), 7.13 (t, J 7.6 Hz, 1H, fluorene), 7.24 (s, 1H, H-αfluorenylidene), 7.40 – 7.27 (m, 3H, fluorene), 7.68 (d, J 7.8 Hz, 2H, fluorene), 7.74 (d, J 7.8 Hz, 2H, fluorene). 13C NMR (75 MHz, CDCl₃) δ (ppm) 27.5, 34.2, 111.3, 114.0, 118.4, 119.5, 119.7, 119.8, 120.4, 124.2, 127.0, 127.1, 128.8, 129.2, 131.7, 136.0, 137.1, 138.7, 139.3, 139.6, 189.6. Anal. Calc. for C₂₁H₁₇N (299.37 g·mol⁻¹): C, 84.25; H, 5.72; N, 4.68. Found: C, 84.35; H, 5.66; N, 4.74%. λ_max (CHCl₃) = 250, 258, 391 nm.

General procedures of the self-condensation reactions

METHOD A. To a solution of starting hetaryl methyl ketone 1a-d (1.0 equiv.) in absolute ethanol (30 mL) tetrachlorosilane (SiCl₄, 2.0 equiv.) was added slowly via the syringe under the inert argon atmosphere at 0 °C. The reaction mixture was left to stir overnight (14 h) at room temperature (25 °C). The dark reaction mixture was poured into ice water (100 mL) and stirred for 10 minutes. The aqueous phase was then extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried (Na₂SO₄). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

METHOD B. To a solution of starting hetaryl methyl ketone 1a-d (1.0 equiv.) in absolute ethanol/anhydrous toluene mixture (50:50) tetrachlorosilane (SiCl₄, 3.0 equiv.) was added slowly via the syringe under the inert argon atmosphere at 0 °C. The reaction mixture was left to stir overnight (14 h) at room temperature (25 °C). The dark reaction mixture was poured into ice water (100 mL) and stirred for 10 minutes. The aqueous phase was then extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried (Na₂SO₄). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

METHOD C. To a solution of starting hetaryl methyl ketone 1a-d (1.0 equiv.) in anhydrous 2-ethoxyethanol (30 mL) tetrachlorosilane (SiCl₄, 4.0 equiv.) was added slowly via the syringe under the inert argon atmosphere at room temperature. The reaction mixture was left to stir overnight (14 h) at room temperature (25 °C). The dark reaction mixture was poured into ice water (100 mL) and stirred for 10 minutes. The aqueous phase was
then extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried (Na₂SO₄). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

METHOD D. To a solution of starting hetaryl methyl ketone 1e and 1f (1.0 equiv.) in anhydrous toluene trifluoromethane sulfonic acid (TFSA, 2.0 mol%) was added slowly via the syringe under the inert argon atmosphere at room temperature (25 °C). The reaction mixture was left to stir for 30 h at 100 °C. Dark reaction mixture was poured to an ice water (100 mL) and stirred for 10 minutes. Water phase was then extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried with Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

1,3,5-Tris-(thien-2-yl)benzene (3a). Yellow solid, after purification on flash flow column chromatography (eluent: CH₂Cl₂). Yield 55% (6.9 g) starting from 2-acetylthiophene 1a (0.039 mol, 4.9 g; SiCl₄: 0.078 mol, 13.25 g, 9.0 mL, Method A, Entry 1, Table 2). Yield 35% (4.4 g), starting from 2-acetylthiophene (1a: 0.039 mol, 4.9 g; SiCl₄: 0.156 mol, 26.5 g, 18.0 mL, Method C, Entry 2, Table 2). Mp 152–156 °C. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.11 (dd, J 3.6 Hz, J 5.1 Hz, 3H, 3 × H-4’-thiophene), 7.34 (dd, J 1.1 Hz, J 6.5 Hz, 3H, 3 × H-3’-thiophene), 7.40 (dd, J 1.1 Hz, J 6.5 Hz, 3H, 3 × H-5’-thiophene), 7.74 (s, 3H, Ar-H benzene: H-2, H-4, H-6). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 122.7, 123.9, 125.4, 128.1, 135.7, 143.5. Anal. Calc. for C₁₈H₁₂S₃ (324.48 g·mol⁻¹): C, 66.63; H, 3.73; S, 13.25 g, 9.0 mL, Method A, Entry 1, Table 2). Yield 58% (8.3 g) starting from 1-(5-methylthien-2-yl)ethanone (5-methyl-2-acetylthiophene) (1b: 0.039 mol, 6.2 g; SiCl₄: 0.078 mol, 13.25 g, 9.0 mL, Method A, Entry 3, Table 2). Mp 136–138 °C. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 2.52 (s, 9H, 3 × CH₃), 6.75 (dd, J 3.4 Hz, J 6.8 Hz, 3H, 3 × H-3’-thiophene), 6.77 (d, J 6.8 Hz, 3H, 3 × H-4’-thiophene), 7.57 (s, 3H, Ar-H benzene: H-2, H-4, H-6). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 155.5, 121.7, 123.6, 126.2, 135.7, 140.1, 141.3. Anal. Calc. for C₁₉H₁₃S₃ (366.56 g·mol⁻¹): C, 68.81; H, 4.95; S, 29.64. Found: C, 69.12; H, 4.80; S, 29.36%. λmax (CHCl₃) 296 nm. The ¹³C NMR and UV-Vis spectra are in accordance with Kotha et al. 1999.³

1,3,5-Tris-(5-chlorothien-2-yl)benzene (3c). Colorless solid, after purification on flash flow column chromatography (eluent: PhMe). Yield 58% (9.7 g) starting from 1-(5-chlorothien-2-yl)ethanone (5-chloro-2-acetylthiophene) (1c: 0.039 mol, 6.2 g; SiCl₄: 0.078 mol, 13.25 g, 9.0 mL, Method A, Entry 4, Table 2). Mp 172–174 °C. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.07 (d, J 6.4 Hz, 3H, 3 × H-4’-thiophene), 7.14 (d, J 6.4 Hz, 3H, 3 × H-3’-thiophene), 7.54 (s, 3H, Ar-H benzene: H-2, H-4, H-6). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 121.9, 123.2, 127.2, 130.1, 135.2, 141.4. Anal. Calc. for C₁₉H₁₃Cl₃S₃ (427.82 g·mol⁻¹): C, 50.53; H, 2.12; S, 22.49. Found: C, 50.62; H, 2.10; S, 22.64%. λmax (CHCl₃) 304 nm. The ¹³C NMR and UV-Vis spectra in accordance with Kotha et al. 1999.³

1,3,5-Tris-(5-bromoacetylthiophen-2-yl)benzene (3d). Colorless solid, after purification on flash flow column chromatography (eluent: PhMe). Yield 28% (6.1 g) starting from 1-(5-bromoacetylthiophen-2-yl)ethanone (5-bromo-2-acetylthiophene) (1d: 0.039 mol, 8.0 g; SiCl₄: 0.117 mol, 20.0 g, 13.5 mL, Method B, Entry 5, Table 2). Mp 112–114 °C. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.07 (d, J 6.8 Hz, 3H, 3 × H-3’-thiophene), 7.14 (d, J 6.8 Hz, 3H, 3 × H-4’-thiophene), 7.54 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 112.4, 122.1, 124.5, 131.1, 135.6, 144.5. Anal. Calc. for C₁₉H₁₃Br₃S₃ (561.17 g·mol⁻¹): C, 38.53; H, 1.62; S, 17.14. Found: C, 38.64; H, 1.80; S, 17.40%. λmax (CHCl₃) 264 nm. The analytical data are in accordance with Cao et al. ⁴⁹

(E)-1,3-Bis-(thien-2-yl)but-2-en-1-one (2a). Pale green-yellow oil, after purification on flash flow column chromatography (eluent: CH₂Cl₂/i-hexane, 50:50). Yield 45% (4.1 g) starting from 2-acetylthiophene (1a: 0.039 mol, 4.9 g; SiCl₄: 0.117 mol, 20.0 g, 13.5 mL, Method B, Entry 6, Table 2). Bp 160–164 °C/4.8 mm Hg; mp 70–74
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(E)-1,3-Bis-(5-methylthien-2-yl)but-2-en-1-one (2b). Pale yellow oil, after purification on flash flow column chromatography (eluent: CH2Cl2/h-hexane, 50:50). Yield 33% (3.4 g) starting from 1-(5-methylthien-2-yl)ethanone (5-methyl-2-acetylthiophene) (1b: 0.039 mol, 5.4 g; SiCl4: 0.117 mol, 20.0 g, 13.5 mL, Method B, Entry 7, Table 2). Bp 132–136°C / 4.8 mm Hg; mp 62–64 °C. 1H NMR (300 MHz, CDCl3) δ (ppm) 2.53 (s, 6H, 2 × CH3), 2.64 (s, 3H, CH3), 6.23 (s, 1H, H-α olefinic), 6.75 (d, J 6.5 Hz, 1H, H-3’ thiophene), 7.07 (d, J 6.5 Hz, 1H, H-4’ thiophene), 7.17 (d, J 6.8 Hz, 1H, H-4’ thiophene), 7.20 (d, J 6.8 Hz, 1H, H-3’ thiophene). 13C NMR (75 MHz, CDCl3) δ (ppm) 15.9, 16.0, 17.5, 121.3, 126.6, 127.8, 128.7, 129.8, 133.6, 142.6, 145.3, 147.7, 148.9, 182.6. Anal. Calc. for C14H14OS2 (303.23 g·mol−1): C, 64.08; H, 5.38; S, 24.44. Found: C, 64.20; H, 5.55; S, 24.75%. λmax(CH2Cl2) 272, 361 nm. The boiling and the melting point are in accordance with Farrar and Levine.50

(E)-1,3-Bis-(5-chlorothien-2-yl)but-2-en-1-one (2c). Pale yellowish oil, after purification on flash flow column chromatography (eluent: PhMe) or by vacuum distillation. Yield 64% (7.5 g) starting from 1-(5-chlorothien-2-yl)ethanone (5-chloro-2-acetylthiophene) (1c: 0.039 mol, 6.2 g; SiCl4: 0.156 mol, 26.5 g, 18.0 mL, Method C, Entry 8, Table 2). Bp 82–86 °C / 4.8 mm Hg; mp 89–92 °C. 1H NMR (300 MHz, CDCl3) δ (ppm) 2.60 (d, J 1.2 Hz, 3H, CH3), 6.91 (d, J 4.2 Hz, 1H, H-α olefinic), 6.94 (q, J 1.2 Hz, J 6.90 Hz, 1H, H-4’ thiophene), 6.96 (d, J 6.2 Hz, 1H, H-4’ thiophene), 7.19 (d, J 6.2 Hz, 1H, H-3’ thiophene), 7.50 (d, J 6.9 Hz, 1H, H-3’ thiophene). 13C NMR (75 MHz, CDCl3) δ (ppm) 17.4, 116.6, 127.3, 127.5, 130.1, 132.5, 139.1, 144.0, 145.8, 147.8, 181.6. Anal. Calc. for C12H8Br2OS2 (303.23 g·mol−1): C, 47.19; H, 2.44; S, 16.35. Found: C, 47.19; H, 2.74; S, 16.34%. λmax(CH2Cl2) 272, 361 nm.

(E)-1,3-Bis-(5-bromothien-2-yl)but-2-en-1-one (2d). Pale yellow-green oil, after purification on flash flow column chromatography (eluent: PhMe) or by vacuum distillation. Yield 31% (4.7 g) starting from 1-(5-bromothien-2-yl)ethanone (5-bromo-2-acetylthiophene) (1d: 0.039 mol, 8.0 g; SiCl4: 0.156 mol, 26.5 g, 18.0 mL, Method C, Entry 9, Table 2). Bp 98–102°C / 4.8 mm Hg; mp 105–107 °C. 1H NMR (300 MHz, CDCl3) δ (ppm) 2.55 (d, J 1.3 Hz, 3H, CH3), 6.95 (q, J 1.3 Hz, 1H, H-α olefinic), 7.05 (d, J 6.2 Hz, 1H, H-4’ thiophene), 7.10 (d, J 6.4 Hz, 1H, H-4’ thiophene), 7.15 (d, J 6.4 Hz, 1H, H-3’ thiophene), 7.45 (d, J 6.2 Hz, 1H, H-3’ thiophene). 13C NMR (75 MHz, CDCl3) δ (ppm) 15.9, 116.8, 127.1, 127.4, 130.2, 130.5, 132.2, 139.8, 140.0, 145.5, 147.9, 182.1. Anal. Calc. for C12H8Br2SO2 (389.84 g·mol−1): C, 37.79; H, 2.06; S, 16.35. Found: C, 38.12; H, 2.44; S, 16.14%. λmax(CH2Cl2) 268, 354 nm.

(E)-1,3-Bis-{5-[(9H-fluorene-9-ylidene)methyl]thiene-2-yl}-but-2-en-1-one (2e). Viscous yellow oil, after purification on flash flow column chromatography (eluent: CH2Cl2). Yield 33% (330 mg). Starting from 1-(5-fluoren-9-ylidinemethylthien-2-yl)ethanone (1e: 1.7 mmol, 500 mg; CF3SO3H: 0.1 mmol, 15 mg, 9.0 μL; Method D, Entry 10, Table 2). 1H NMR (300 MHz, DMSO-d6) δ (ppm) 2.65 (s, 3H, CH3), 6.85 (s, 1H, Hfluorenylidene), 6.95 (s, 1H, Hfluorenylidene), 7.05 (q, J 1.3 Hz, 1H, H-α olefinic), 7.30 (d, J 7.9 Hz, 2H, H-3’ thiophene, H-3” thiophene), 7.83–7.72 (m, 8Hfluorene), 7.89 (d, J 7.7 Hz, 2H, H-4’ thiophene, H-4” thiophene), 8.00–8.19 (m, 8Hfluorene). 13C NMR (75 MHz, DMSO-d6) δ (ppm) 18.2, 117.6, 118.5, 118.7, 119.5, 119.9, 120.1, 120.5, 120.7, 123.9, 124.0, 126.9, 127.1, 128.5, 128.6, 128.7, 129.2, 131.2, 131.7, 131.9, 134.8, 134.9, 138.1, 138.3, 138.6, 138.9, 140.7, 140.9, 145.9, 146.7, 147.3, 181.7. Anal. Calc. for C40H36O2S (586.76 g·mol−1): C, 81.88; H, 4.47; S, 10.93. Found: C, 82.12; H, 5.00; S, 10.87%. λmax(CHCl3) 251, 259, 468 nm.
Viscous yellow, after purification on flash flow column chromatography (eluent: CH$_2$Cl$_2$). Yield 33% (326 mg). Starting from 1-{5-[(9H-fluorene-9-ylidene)methyl]-1-methyl-1H-pyrrole-2-yl}ethanone (1f: 1.7 mmol, 510 mg; CF$_3$SO$_3$H: 0.1 mmol, 15 µL; Method D, Entry 11, Table 2). 1H NMR (300 MHz, DMSO-d$_6$) $\delta$ (ppm) 2.55 (s, 3H, CH$_3$), 3.46 (s, 6H, 2 × CH$_3$), 6.45 (d, $J$ 3.9 Hz, 3H, 1 × H-$\alpha$olefinic, 2 × H$_{fluorenylidene}$), 6.83 (d, $J$ 6.9 Hz, 2H, H-$4''$pyrrole, H-$4''$pyrrole), 7.21 (d, $J$ 6.9 Hz, 2H, H-$3'$pyrrole, H-$3''$pyrrole), 7.37–7.33 (m, 8H, 8 × H$_{fluorene}$), 7.78–7.73 (m, 8H, 8 × H$_{fluorene}$). 13C NMR (75 MHz, DMSO-d$_6$) $\delta$ (ppm) 24.2, 32.2, 110.9, 112.8, 112.9, 116.7, 119.8, 119.9, 120.1, 126.9, 127.7, 128.3, 131.4, 132.3, 136.4, 136.5, 139.6, 140.7, 182.0. Anal. Calc. for C$_{42}$H$_{32}$N$_2$O (580.72 g·mol$^{-1}$): C, 86.87; H, 5.55; N, 4.82. Found: C, 86.53; H, 5.34; N, 4.67%. $\lambda$$_{max}$ (CHCl$_3$) 252, 261, 460 nm.

1,3-Bis-(thien-2-yl)-5-(4-fluorophenyl)benzene (4). To a solution of (E)-1,3-bis-(2-thienyl)but-2-en-1-one (2a, 1.22 mmol, 290 mg) and 4'-fluoroacetophenone (1.22 mmol, 168.5 mg, 148 µL) in anhydrous toluene (5 mL) the tetrahydrate of erbium triflate [Er(OTf)$_3$·4H$_2$O, 0.12 mmol, 81.0 mg] was added. The mixture was stirred at the boiling point of toluene (110 °C) for 6 h (Scheme 3). Reaction mixture was poured to a water (10 mL). Water phase was extracted with toluene (3 × 15 mL). Collected organic layers were washed with water (2 × 10 mL), saturated solution of NaCl (2 × 10 mL) and then dried (Na$_2$SO$_4$). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (eluent: n-hexanes). Yield 62% (254 mg) of cream-yellow solid. Mp 208-211 °C. 1H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 7.17 (t, $J$ 6.6 Hz, 2H, H-$4'$thiophene, H-$4''$thiophene), 7.22 (t, $J$ 1.9 Hz, J 6.6 Hz, 2H, H-$4'$thiophene, H-$4''$thiophene), 7.37 (s, 2H, ArH, H-1 benzene, H-6 benzene), 7.58 (d, $J$ 6.6 Hz, 2H, H-$3'$thiophene, H-$3''$thiophene), 7.70 (d, $J$ 6.6 Hz, 2H, H-$5'$thiophene, H-$5''$thiophene), 7.71 (J 3.7 Hz, 2H, H-$2''$benzene, H-$6''$benzene), 7.92 (d, $J$ 3.7 Hz, 2H, H-$3''$benzene, H-$5''$benzene), 8.21 (s, 1H, ArH, H-1 benzene). 13C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) 118.4, 124.6, 137.7, 145.9, 153.4, 154.7, 165.9, 175.6, 178.9, 198.7, 198.9. For C$_{20}$H$_{13}$FS$_2$ (336.45 g·mol$^{-1}$) (ESI) m/z 337.14 [M+H$^+$].

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