Extended π Systems

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Rigid Conjugated Twisted Truxene Dimers and Trimers as Electron Acceptors

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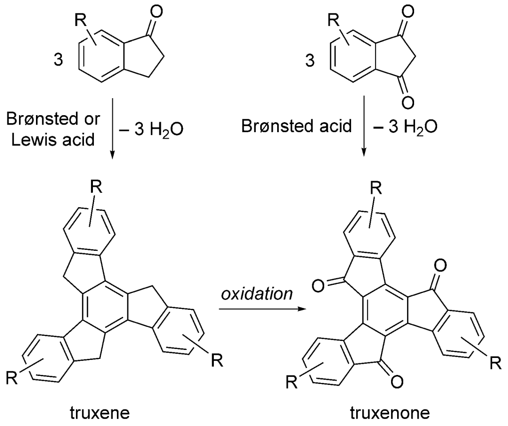
Abstract: *A new class of rigid twisted truxenone oligomers with an enlarged π backbone has been established by oxidative dimerization reactions. The resulting extended conjugated systems have large extinction coefficients and low-lying LUMO levels and show good solubility in common organic solvents, thus making them attractive compounds as new electron acceptors in organic electronics. Their suitability as electron acceptors has been demonstrated in bulk-heterojunction organic solar cells with poly({4,8-bis[(2-ethylhexyl)oxy]-benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) as the donor material.*

The acid-catalyzed trimerization of indanones to truxenes by two subsequent aldol condensation reactions and a final electrocyclization and condensation step was first described by Kipping in 1894 (Scheme 1).[1] This reaction gives the products usually in high yields when some guidelines concerning the reaction conditions are followed.[2] Similarly, 1,3-indanediones can be converted in condensation reactions into the corresponding truxenones (Scheme 1).[3] Owing to their symmetry and the conjugated π system, derivatives of both types of compounds, truxenes as well as truxenones, are attractive for supramolecular and materials chemistry.[4]



Scheme 1. Methods for the synthesis of truxenones.

Some truxenone derivatives are difficult to synthesize by the condensation of the indanedione precursor, especially with a certain substitution pattern in the periphery. It is synthetically more convenient to transform the corresponding truxenes into the truxenones by oxidation of the benzylic fluorene positions.[5,6] For example, Pei and co-workers found during studies towards the etherification of trihydroxytruxenes with *n*-hexyl bromide that the corresponding truxenones formed in moderate to good yields instead of the O-alkylated truxenes.[5a,b] During this study they found that trialkoxy truxenes can be converted in sufficient yield into the truxenones with tetramethylammonium hydroxide and oxygen in THF. Recently, a mixture of KOH and graphene at room temperature in air was used to oxidize truxene to truxenone in 93 % yield.[5c] During our ongoing research on the conversion of truxenes into truxenones, we found an unprecedented oxidative dimerization reaction that connected two or three truxenes at benzylic fluorene positions through a highly strained double bond.

Initially, a simple protocol for the conversion of truxenes into truxenones with KOH in THF under exposure to air was used.[6h] For example, when truxene **1a** was oxidized by KOH/THF/air (method A in Table 1), the reaction was barely reproducible, and the yields for the isolated truxenone **2a** were in the range of 37–87 %. Similar results were observed for truxenone **2b**, with yields in the range of 19–29 %, and the mesityl-substituted truxenone **2c** (19 % yield). Therefore, we applied an alternative method and used benzyltrimethylammonium hydroxide (Triton B) as the base and O_2 as the oxidant in pyridine as solvent.[6b] Indeed, by using this protocol (method B in Table 1), we obtained truxenone **2a** reproducibly in 79 %, and the yields of truxenones **2b** and **2c** were with 81 % and 54 % also significantly higher than for reactions performed by method A.

However, when method B was applied for the oxidation of nitrotruxene **3** under same conditions, a substantial amount (13 %) of a truxene dimer (**5**) was formed as a dark-purple solid besides the truxenone **4** (59 % yield) (Scheme 2). By carrying out the reaction with a higher concentration of truxene **3** (77.4 mM), the yield of the dimer **5** could be significantly increased to 37 % and the amount of truxenone **4** decreased to 24 %. If molecular oxygen was substituted by more benign air under the same conditions, the yield of dimer **5** was maximized to 44 %, and again the formation of

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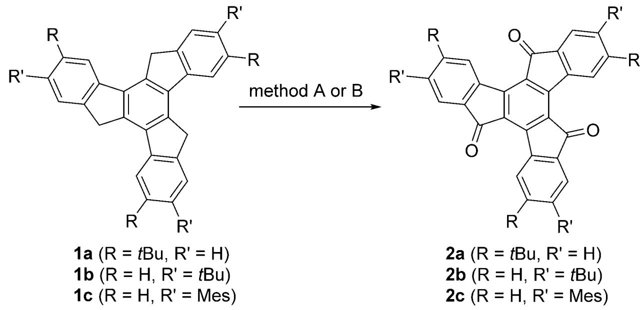
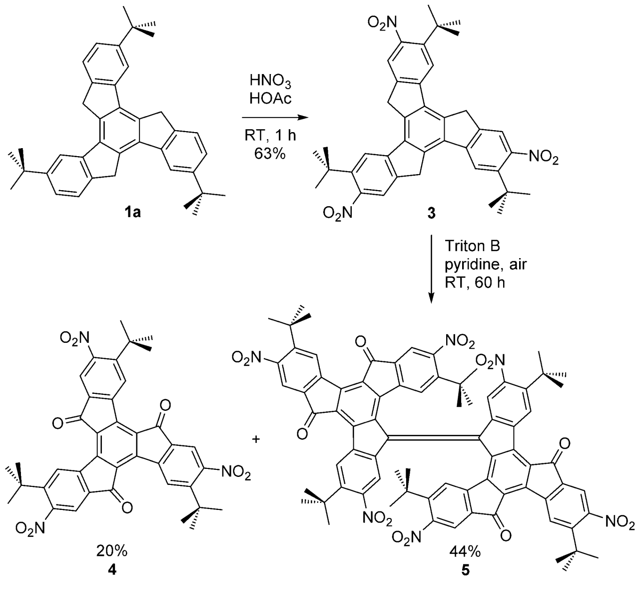
Table 1: Oxidation of truxenes **1 a**–**c**[7a–c] to truxenones **2 a**–**c**.



Entry	Truxene	Method[a]	Yield of **2** [%][b]
1	**1 a**	A	37–87
2	**1 a**	B	79
3	**1 b**	A	19–29
4	**1 b**	B	81
5	**1 c**	A	18
6	**1 c**	B	54

[a] Method A: KOH, THF, air, room temperature, 48 h; method B: Triton B, pyridine, O_2, room temperature, 48 h. [b] Yield of the isolated product. Mes = 2,4,6-trimethylphenyl.

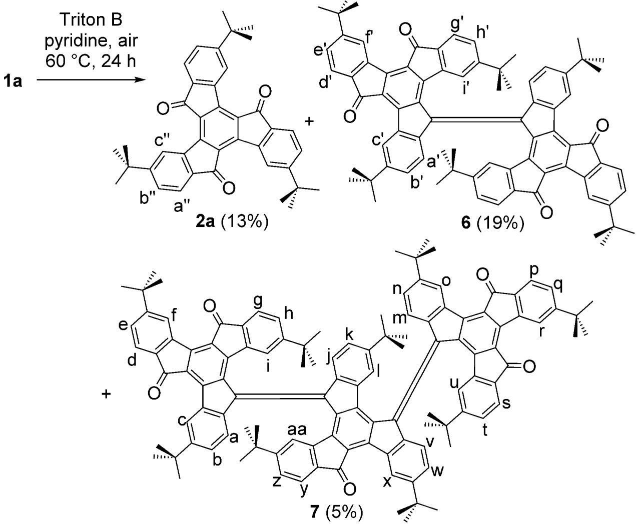


Scheme 2. Synthesis of nitrotruxene **3** and subsequent oxidation with Triton B and oxygen or air.

monomer **4** was slightly decreased. By ultraperformance liquid chromatography (UPLC)–MS analysis of the crude product, the formation of a trimeric species was detected (*m/z* 1998; see the Supporting Information); however, owing to its very low solubility, it was not possible to isolate and purify this side product by column chromatography or HPLC.

Dimer **5** was fully characterized by NMR, MS, IR, and UV/Vis spectroscopy and further by single-crystal X-ray diffraction (see Figure 1). Suitable single crystals were obtained from deuterated chloroform. The compound crystallized as a racemate with two molecules in the unit cell of the monoclinic space group *P*-1.

The internal *E*-configured bifluorenylidene double bond, which connects the two truxene subunits, is with 1.388 Å relatively long.[8] Furthermore, the two bifluorenylidene units attached to the internal double bond deviate from planarity, and the double bond is highly twisted with torsional angles between 34 and 35°.[9] The molecules are densely packed by a large number of weak intermolecular interactions, such as π–π stacking and interactions of the nitro groups in either an anion–π-type fashion with the π planes of the truxene or through hydrogen bonding of the nitro groups to aromatic hydrogen atoms.



Scheme 3. Oxidation of truxene **1 a** with Triton B and air to give truxenone **2 a**, dimer **6**, and trimer **7**.

Encouraged by the increased accessible amount of dimer **5**, we reinvestigated the oxidation of truxene **1 a** at a higher concentration (98 mM) and in air (Scheme 3). At room temperature, the main product was still the truxenone **2 a**, but dimer **6** could also be isolated, although only in 5 % yield. At elevated temperature (60 °C) the formation of dimer **6** was increased to 19 % and that of monomer **2 a** reduced to 13 %. Most interestingly, trimer **7** formed in this reaction was soluble enough to be isolated in 5 % yield by a combination of silica-gel column chromatography and size-exclusion chromatography. The monomer **2 a**, dimer **6**, and trimer **7** showed distinct patterns and well-resolved peaks in the ^{1}H NMR spectra (Figure 2). Most characteristic are the patterns for the hydrogen atoms in the fjord regions, which are shifted upfield as a result of the through-space deshielding effect of the carbonyl oxygen atoms. For the C_{3v}-symmetric truxenone **2 a**, these protons ($H^{c''}$) resonate at $\delta = 9.34$ ppm. Dimer **6** has C_{2v} symmetry and therefore two such fjord protons ($H^{c'}$ and $H^{f'}$) are magnetically different, resonating at $\delta = 9.63$ and 9.53 ppm. For trimer **7**, five signals at $\delta = 9.75$, 9.69, 9.63, 9.56, and 9.52 ppm can be found for the fjord protons, owing to the inherent C_1 symmetry. Dimer **6** was additionally

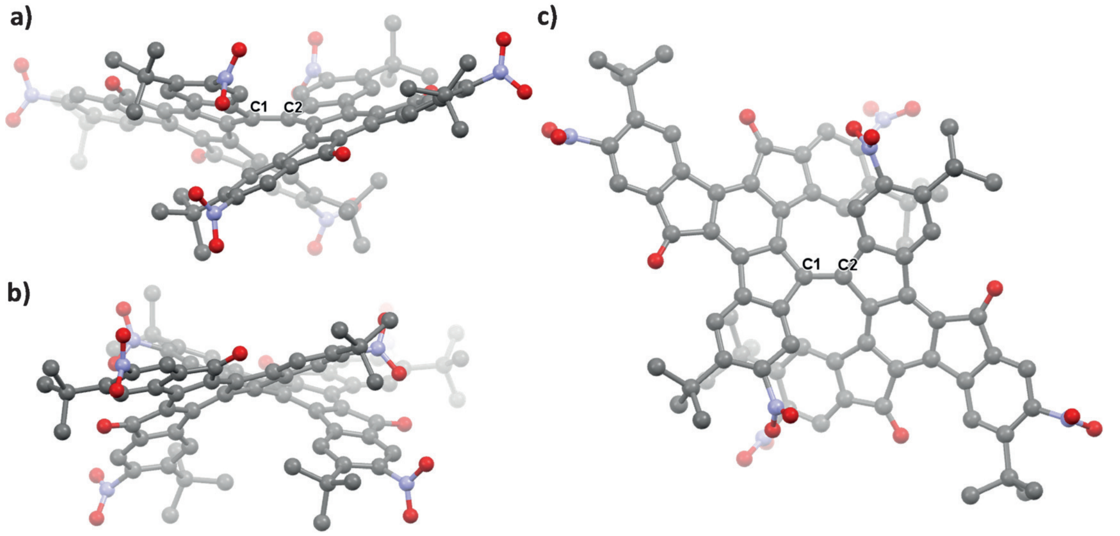


Figure 1. Crystal structure of **5**. a, b) Side views; c) top view. The hydrogen atoms are omitted for clarity. The atoms of the internal double bond are labeled C1 and C2. Please note, only the *P* enantiomer of the racemic crystal is depicted.

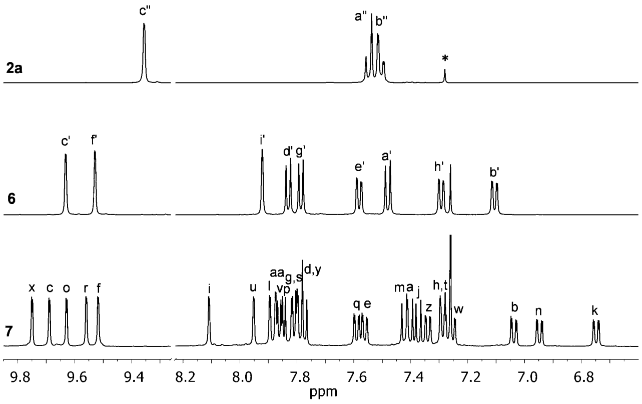


Figure 2. Partial ^{1}H NMR spectra (500 MHz, CDCl$_3$) of truxenone monomer **2a**, dimer **6**, and trimer **7**. For the assignment of the peaks, see molecular structures in Scheme 3. Full NMR spectra can be found in the Supporting Information.

characterized by single-crystal X-ray diffraction (see the Supporting Information). In the single-crystal structure of **6**, clear deviations of the truxene π planes from planarity could be detected, as for **5**.

Whereas truxenones **2a** and **4** were yellow, the dimers **5** and **6** were deep-purple in solution, which immediately reminded us of the color of C$_{60}$. In the UV/Vis spectra of dimers **5** and **6** in chloroform, broad peaks with maxima at $\lambda_{max} = 577$ and 581 nm, respectively, appeared, which were not present in the spectra of the smaller truxenones **2a** and **4** and most probably can be assigned to π–π* transitions (Figure 3 and Table 2). Trimer **7** was blue, and again a broad absorption peak at $\lambda_{max} = 596$ nm was detected.

The compounds were also investigated by cyclic voltammetry (see Figure 3 and Table 2). Dimer **5** showed two quasireversible reduction waves at $E_{1/2}^{red(1)} = -0.67$ V and $E_{1/2}^{red(2)} = -1.04$ V and one irreversible oxidation wave at $E_{1/2}^{ox} = +1.36$ V. The values correspond to $E_{LUMO} = -4.2$ eV and $E_{HOMO} = -6.1$ eV, thus the gap between HOMO and LUMO is $E_g = 1.9$ eV and correlates well with that determined from the onset of the UV/Vis spectrum ($E_{g,opt} =$

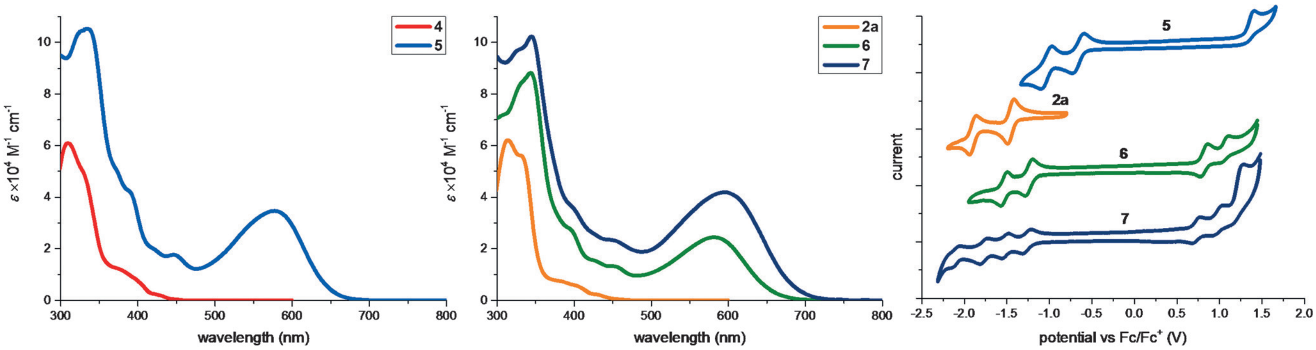


Figure 3. UV/Vis spectra (measured in CHCl$_3$) of monomers **2a**, **4**, dimers **5**, **6**, and trimer **7** and cyclic voltammograms (measured in CH$_2$Cl$_2$/ 0.1 M [nBu$_4$N]$^+$[ClO$_4$]$^-$ at 0.1 V s^{-1}) for **2a**, **5**, **6**, and **7**.

Table 2: Summary of the photophysical and electrochemical characterization of compounds **2a** and **4**–**7**.

Compd	λ_{abs} $(\log \varepsilon)$[a] [nm]	E_g [eV]	$E_{1/2}^{\text{red}}$[b,c] [V]	$E_{1/2}^{\text{ox}}$[b,c] [V]	E_{LUMO}[d] [eV]	E_{HOMO}[e] [eV]
2a	314(4.79), 332(4.75), 383(3.85), 405(3.70), 413(3.28)	2.78[f]	−1.45, −1.89	–	−3.41	−6.19[g]
4	309(4.798), 333(4.67), 378(4.61), 428(3.34)	2.82[f]	–[h]	–[h]	–	–
5	335(5.02), 372(4.70), 393(4.61), 446(4.25), 577(4.54)	1.91[f] 1.87[i]	−0.67, −1.04	1.36	−4.22	−6.09
6	328(4.92), 343(4.95), 398(4.42), 428(4.18), 455(4.11), 581(4.39)	1.88[f] 1.89[i]	−1.24 −1.53	0.82, 1.08	−3.66	−5.55
7	324(4.98), 345(5.01), 401(4.55), 453(4.37), 596(4.62)	1.81[f] 1.85[i]	−1.27, −1.53, −1.77, −2.09	0.73, 1.00, 1.22	−3.62	−5.47

[a] Measured in $CHCl_3$ at room temperature. [b] Measured in CH_2Cl_2 with Bu_4NClO_4 as the electrolyte. [c] Calculated against the internal standard for Fc/Fc^+. [d] $E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{red}} + 4.8\ \text{eV})$. [e] $E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.8\ \text{eV})$. [f] Estimated from the absorption onset. [g] $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g,opt}}$. [h] Not detected owing to poor solubility. [i] Calculated from CV measurement.

1.9 eV). In comparison to the nitro-substituted dimer **5**, the "nonsubstituted" dimer **6** also showed two quasireversible reduction waves, but at substantially lower potentials ($E_{1/2}^{\text{red(1)}} = -1.24$ V and $E_{1/2}^{\text{red(2)}} = -1.53$ V). In contrast to **5**, for **6** two oxidation waves were found at $E_{1/2}^{\text{ox(1)}} = +0.82$ V and $E_{1/2}^{\text{ox(2)}} = +1.08$ V. Although the band gap ($E_g = 1.9$ eV) is very similar, both HOMO and LUMO levels are higher in energy owing to the lack of the electron-withdrawing nitro groups and are found at $E_{\text{LUMO}} = -3.7$ eV and $E_{\text{HOMO}} = -5.5$ eV. For trimer **7**, as many as four quasireversible reduction waves were determined, as well as three oxidation waves. The HOMO and LUMO levels ($E_{\text{LUMO}} = -3.6$ eV and $E_{\text{HOMO}} = -5.5$ eV) are comparable with those of the dimer **6**, which is also in agreement with the energy gap estimated by the onset in the UV/Vis spectra.

The optical as well as electrochemical data revealed that these compounds might be used as electron-acceptor compounds in bulk-heterojunction organic solar cells (BHJOSCs) instead of fullerene derivatives.[10,11] For preliminary tests, PTB7 was used as the donor material in an inverse device setup (ITO/ZnO/PTB7:truxene dimer **6**/MoO_3/Ag), which we used previously with aroylenimidazole derivatives (see also the Supporting Information).[12] A first screening revealed that a photovoltaic device with a 1:2 donor/acceptor ratio gave an open-circuit voltage of $V_{\text{OC}} = 1.04$ V, a short-circuit current of $J_{\text{SC}} = -7.16$ mA cm^2, and a fill factor of 40.3 %, thus resulting in an overall device performance with a power-conversion efficiency (PCE) of 3.0 %, which is significantly higher than that of previously reported BHJ devices based on monomeric truxene derivatives.[13a,b] In contrast to the results for dimer **6**, a very first photovoltaic device with truxene trimer **7** as the acceptor gave under the same conditions a significantly lower PCE of 1.2 %. However, these results clearly demonstrate that this new class of truxene oligomers are promising candidates as non-fullerene acceptors, and further optimization studies will be pursued in due course.[11–13]

To summarize, we have found an unprecedented oxidative dimerization reaction of truxenes, in which a twisted and elongated double bond between former benzylic positions was created to form bifluorenylidene subunits.[14] The compounds are highly twisted and, similar to other twisted aromatic compounds, highly soluble in organic solvents (e.g. **6** in chloroform: 70 mg mL^{-1}, **7** in chloroform: 58 mg mL^{-1}).[10] Owing to the uptake of up to two or four electrons, the similarity of their E_{LUMO} value of around −3.7 eV to those of C_{60} derivatives, and their good light-absorption properties as well as their good solubility, these compounds are attractive as non-fullerene acceptors for further studies,[11,12a,b] as has been demonstrated by preliminary tests with PTB7 as a donor in BHJOSCs giving a PCE value of 3.0 %. Furthermore, the remaining keto functions in **6** and **7** could be converted into dicyanovinylene units[3a,13] to further adjust energy levels, absorption properties, and charge-transport behavior.

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