DOI: 10.1002/adsc.201601331

Advanced Synthesis & Catalysis

Very Important Publication

Efficient Oxidative Coupling of Arenes *via* Electrochemical Regeneration of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) under Mild Reaction Conditions

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Received: December 2, 2016; Revised: January 23, 2017; Published online: ■■ ■■, 0000

Supporting information for this article can be found under http://dx.doi.org/10.1002/adsc.201601331.

Abstract: The intramolecular dehydrogenative carbon-carbon bond formation of aromatic rings in the presence of catalytic amounts of an oxidising agent is herein described. The oxidative coupling is realised under indirect anodic conditions, utilising 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an efficient redox mediator under acidic conditions. In comparison, for the stoichiometric oxidative coupling reaction of hexakis(4-*tert*-butylphenyl)benzene on a 1.0 gram scale, 1.56 g of DDQ were applied, whereas in the present indirect electrochemical version, only 15 mg of DDQ were needed, resulting in significantly easier purifications of the products. The reaction proceeds smoothly using a variety of polyaromatics including terphenyl, quaterphenyl and heptaphenyl derivatives to give polyphenylenes in excellent yields and current efficiencies. A detailed optimisation study, investigations on the electrochemical behaviour of the redox mediator and synthetic applications of the method are discussed.

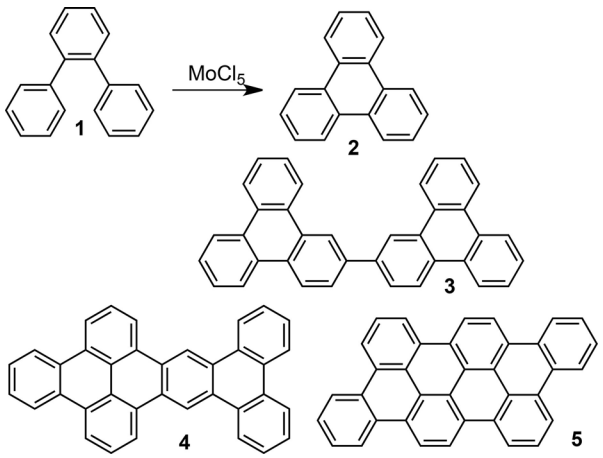
Keywords: C–C coupling; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); electrochemistry; oxidation; oxidative coupling; polycyclic aromatic hydrocarbons

Introduction

The direct dehydrogenative coupling of two arenes, the so-called Scholl reaction, has been accomplished by various methods for the preparation of polycyclic aromatic hydrocarbons (PAHs).[1] The advantage of this method is that no pre-functionalisation is required and it serves as a straightforward, atom and reaction step economical method, in contrast to cross-coupling methodologies (Suzuki–Miyaura, Stille, Kumada, Negishi) using transition metal catalysts.[2]

Two reaction mechanisms of the Scholl reaction have been proposed and the dispute whether arenium cations or radical cations are the reactive intermediates has been thoroughly discussed.[3]

Generally, the carbon-carbon bond formations are most efficient when electron-rich arene derivatives are used and a pre-orientation of the aromatic rings, such as in *ortho*-terphenyls, allows the access to larger aromatic ring systems.[3d] In a seminal work, King and co-workers described the oxidative coupling reaction of a simple *ortho*-terphenyl **1** (Scheme 1) and the problems associated with this seemingly simple transformation. Besides the desired triphenylene product **2**, also dimers of **2** either connected *via* a carbon-carbon single bond (**3**) or condensed products (**4**/**5**) were identified.[3c] The number of side products can be efficiently reduced by the introduction of directing groups, such as alkoxy groups, or by the introduction



Scheme 1. Oxidative coupling reaction of *ortho*-terphenyl and identified side products reported by King.

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of bulky substituents, such as *tert*-butyl groups to block positions on the arene rings.

In addition, the electronic nature of the arene is an important factor since electron-deficient arenes do not undergo this carbon-carbon bond formation either because of their higher redox potentials or their lower nucleophilicities.[4] Moreover, if mixtures of different substrates are used homo-dehydrodimers have been found in significant amounts. This reveals the complex relationship between the redox potential and the nucleophilicity of each substrate.[5]

Originally, the Scholl reaction was performed using strong Lewis and Brønsted acids and high reaction temperatures resulting in many side products.[6]

Moreover, the intramolecular coupling of electron-rich polyaromatic systems under direct electrochemical oxidation was investigated by Hammerich and Parker yielding a large variety of Scholl products.[7] Another approach has been reported by Waldvogel on the electrochemical phenol-arene cross-coupling using boron-doped diamond electrodes (BDD) where the selective generation of a phenoxyl radical intermediate plays a crucial role.[8] An intermolecular arene-arene cross-coupling reaction has been reported by Yoshida relying on a selective electrochemical oxidation and accumulation of one reaction partner at low temperature ("radical-cation-pool method") which can react then with a second non-activated arene.[9]

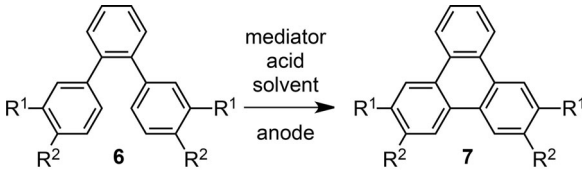
Furthermore, a large number of strong oxidising agents has been reported to accomplish these oxidative coupling reactions, such as $CuCl_2$ or $Cu(OTf)_2$ and $AlCl_3$,[10a,b] $Tl(O_2CCF_3)_3$ in CF_3CO_2H,[10c] $Pb(OAc)_4/BF_3{\cdot}OEt$,[10d] Hg(II) salts,[10e] VOF_3,[10f] $SbCl_5$,[10g] Meerwein's reagent,[10h] $FeCl_3$[10i] and $MoCl_5$.[1c,10j] Although good results could be achieved, a significant drawback is that many of those oxidants have to be used in over-stoichiometric amounts. Thereby, large amounts of toxic chemical waste and often chlorinated side products are encountered giving rise to ecological problems. Metal-free oxidants such as hypervalent iodine compounds[11] or quinones seem to be less problematic. Therefore, Rathore reported the use of stoichiometric amounts of DDQ (2,3-dichloro-4,5-dicyano-*para*-benzoquinone) in acidic solution for the synthesis of polymethoxylated triphenylenes.[3d,10h,12] Although DDQ was reported to be recyclable after isolation,[12,13] we are unaware of an *in situ* recycling process utilising DDQ in only catalytic amounts in oxidative coupling reactions.

Many examples for the reversible redox behaviour of quinones have been reported in the literature and many chemical co-oxidants are known for the regeneration of DDQ in organic reactions.[14] Electrolysis represents hereby a promising environmentally benign method for the *in situ* oxidation of $DDQH_2$. However, examples in which DDQ has been used as electrochemical redox mediator are rare.[15]

For a long time, our group has been interested in the efficient synthesis of functionalised poly-aromatic hydrocarbons using transition metal catalysts[16] as well as their use for surface applications.[17] Also, we have reported the Scholl reaction for the synthesis of oligoarenes some time ago.[18] In this respect, we decided to investigate an electrochemical intramolecular arene-arene coupling using DDQ as mediator under oxidative electrochemical reaction conditions, which we report herein.

Results and Discussion

To explore the reaction, we selected tetramethoxy-*ortho*-terphenyl **6a** and dimethoxy-*ortho*-terphenyl **6b** as model substrates (Scheme 2).



6a: R^1 = OMe; R^2 = H
6b: R^1 = OMe; R^2 = OMe

original conditions: Bu_4NBF_4 (0.3 M); CH_2Cl_2, H_3CSO_3H, r.t., carbon fiber electrode, divided cell

Scheme 2. Oxidative coupling of *ortho*-terphenylenes **6a/b** under electrochemical conditions.

At first, cyclic voltammetry was performed to understand the electrochemical behaviour of DDQ under the original reaction conditions reported for the oxidative coupling.[12] The cyclic voltammogram (CV) of $DDQ/DDQH_2$ (Figure 1, curve a) exhibits two reversible redox potentials for the semiquinone and the quinone at −0.21 V and 0.64 V *vs.* Ag/AgCl when 0.1 M Bu_4NBF_4/CH_2Cl_2 was used as supporting electrolyte. When methanesulfonic acid was added (curve b) the potentials for the oxidation were shifted towards more positive oxidation values of 0.76 V and 1.10 V (determined *via* differential pulse voltammetry measurements, see the Supporting Information).

For the reductive process, the semiquinone reduction potential shifted towards more positive potentials and merged into one wave (0.80 V). A similar behaviour is well established for quinoid redox systems.[19] As shown in Figure 1, the anodic peak current for DDQ increases compared to curve b when an excess of **6a** is present. Since substrate **6a** is not oxidised at those potentials (curve d), the increase in anodic current results from its re-entering the catalytic oxidation cycle. This observation is clear evidence that DDQ

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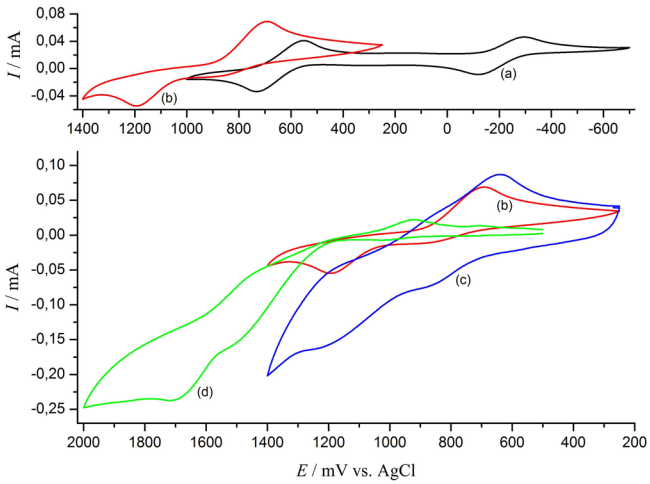

Figure 1. Cyclic voltammogram of DDQ (2.2 mm): a) in CH_2Cl_2/Bu_4NBF_4 (10 mL, 0.1 M); b) with H_3CSO_3H as additive (CH_2Cl_2:H_3CSO_3H = 9:1); c) with H_3CSO_3H as additive (CH_2Cl_2:H_3CSO_3H = 9:1) and **6a** (15 mg, 51.7 µmol); d) only **6a** (15 mg, 51.7 µmol) in CH_2Cl_2/Bu_4NBF_4 (10 mL, 0.1 M). Reference electrode: Ag/AgCl (KCl_{sat}), scan rate = 100 mV s^{-1}.

acts as mediator and that $DDQH_2$ is regenerated after oxidation of substrate **6a**.

In a series of experiments, we screened various reaction conditions, such as different commercially available *para*-quinones (Table 1, entries 1–4), we modified the acid additive (entries 5–10) and varied the solvent (entries 11–13).

The indirect anodic oxidation was conducted in a divided cell equipped with carbon fibre electrodes (see the Supporting Information) at room temperature applying a current of 10 mA.

At first, we conducted the synthesis of **7b** under standard conditions of the oxidative coupling reported for DDQ, but under electrochemical regeneration of the redox agent. The desired product could be obtained in a moderate yield of 69% with a good current efficiency of 60% (entry 1). When using 2,6-dichloro-*p*-benzoquinone or *p*-chloranil as redox mediator the product was obtained in lower yield and current efficiency (entries 2 and 3). In the absence of a redox mediator, the product was also formed but the yield was much lower and the reaction time was twice as long (entry 4).

A strong influence on yield and current efficiency was found by varying the acid additive. While the use of trifluoromethanesulfonic acid, *p*-toluenesulfonic acid and acetic acid resulted in a lower yield compared to methanesulfonic acid, the use of trifluoroacetic acid gave product **7b** in an excellent yield of 92% and 91% current efficiency (entries 5–8). Aqueous acetic acid as well as sulfuric acid gave no product, presumably due to their poor solubility in dichloromethane (entries 9 and 10). It is noteworthy that under non-electrochemical reaction conditions no dependency between the acid additive and the product yield was determined.

Changing the solvent to acetonitrile or methanol did neither improve the chemical yield nor the current efficiency. However, the fact that both solvents are also suitable may be important for substrates that are insoluble in dichloromethane (entries 11 and 12). In contrast, the use of DMSO as solvent resulted in no conversion, neither the DDQ-mediated reaction nor the direct oxidation of **6b** took place (entry 13). A considerable advantage of the present protocol is that the transformation can be conducted without

Table 1. The effects of redox mediator, acid additive and solvent on the electrochemical synthesis of **7b**.[a]

Entry	Mediator	Acid	Solvent	Yield[b]/(ce)[e]
1	DDQ	H_3CSO_3H	CH_2Cl_2	69% (60%)
2	2,6-dichloro-*p*-benzoquinone	H_3CSO_3H	CH_2Cl_2	65% (55%)
3	*p*-chloranil	H_3CSO_3H	CH_2Cl_2	62% (52%)
4	none	H_3CSO_3H	CH_2Cl_2	54% (25%)
5	DDQ	F_3CSO_3H	CH_2Cl_2	84% (77%)
6	DDQ	*p*-TsOH	CH_2Cl_2	67% (56%)
7	DDQ	H_3CCO_2H	CH_2Cl_2	75% (41%)
8	DDQ	F_3CCO_2H	CH_2Cl_2	92%[c] (91%)
9	DDQ	H_3CCO_2H/H_2O[d]	CH_2Cl_2	–
10	DDQ	H_2SO_4	CH_2Cl_2	–
11	DDQ	F_3CCO_2H	CH_3CN	84% (67%)
12	DDQ	F_3CCO_2H	MeOH	88% (65%)
13	DDQ	F_3CCO_2H	DMSO	–

[a] *Reaction conditions:* terphenyl **6b** (58 mg, 165 µmol, 1.0 equiv.), mediator (5 mol%), Bu_4NBF_4 (1.00 g/chamber, 0.3 M), solvent/acid (10 mL/chamber, 9:1 v/v), carbon fibre electrodes, H-type cell, 10 mA, room temperature.
[b] Yields were determined by ^1H NMR analysis using mesitylene as internal standard.
[c] Isolated yield.
[d] Solvent ratio: 5.5:4.5 (v/v).
[e] ce: current efficiency.

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strict exclusion of water and air and without encountering any loss in yield or current efficiency.

Next, we focused upon parameters such as the electrode material, the cell type, the current density and the amount of redox mediator (Table 2 and Table 3).

Table 2. Effects of the electrode material and cell type on the formation of **6b**.[a]

No	Mediator loading	Cell type	Yield[b]/(ce)[c]
1	Pt plate	H-type	89% (91%)
2	glassy carbon	H-type	89% (75%)
3	BDD	H-type	91% (89%)
4	graphite	H-type	(decomp. of anode)
5	graphite felt	H-type	55% (37%)
6	Pt plate[e]	undivided cell	66% (28%)

[a] *Reaction conditions:* terphenyl **6b** (58 mg, 165 µmol, 1.0 equiv.), DDQ (5 mol%), Bu_4NBF_4 (1.00 g/chamber, 0.3 M), CH_2Cl_2/H_3CCO_2H (10 mL/chamber, 9:1 v/v), electrodes, cell type, 10 mA, room temperature.
[b] Yields were determined by ^1H NMR analysis using mesitylene as internal standard.
[c] ce: current efficiency.

As shown in Table 2, excellent yields of **7b** were obtained when carbon fibre, platinum, glassy carbon and BDD (boron-doped diamond) electrodes were used as anode material (entries 1–3). Merely graphite and graphite felt led to low yields and low current efficiencies and, in addition, decomposition of the electrode material was observed during the reaction (entries 4 and 5). Using an undivided cell type, equipped with platinum plate electrodes (25 × 10 mm) resulted in a lower yield (several not identified side products were observed) and increased reaction times, presumably due to a competing reductive processes (entry 6).

Next, investigations concerning different applied currents and redox mediator loadings were conducted with 2,7-dimethoxytriphenylene (**6a**) as substrate. This change in substrate was undertaken because the starting material has a higher redox potential and therefore undergoes no direct oxidation (Table 3, entry 1). Noteworthy, the reaction could also be performed on a two gram scale without any loss of yield. The yield is hereby much higher in comparison with those of classical oxidative coupling reactions using over-stoichiometric amounts of DDQ/$MeSO_3H$ (58%),[20] $FeCl_3$ (64%)[21] or $MoCl_5$ (53%).[3c] Merely a modified $MoCl_5$/HFIP system reported by Waldvogel gave a similar good yield (89%).[22]

Applying higher currents resulted in lower yields and longer reaction times (Table 3, entries 2 and 3). The same loss in yield was observed by reducing the redox mediator loading and the formation of new unidentified side products was observed (entries 4–6).

Table 3. Effects of the applied current and mediator loading on the electrochemical synthesis of **6a**.[a]

No	Mediator loading	Current	Yield[b]/(ce)[d]
1	none	10 mA	–
2	5 mol%	10 mA	85%[c] (82%)
3	5 mol%	20 mA	57% (41%)
4	5 mol%	40 mA	n.d.
5	2.5 mol%	10 mA	79% (72%)
6	1 mol%	10 mA	66% (55%)

[a] *Reaction conditions:* terphenyl **6a** (52 mg, 180 µmol, 1.0 equiv.), DDQ (1–5 mol%), Bu_4NBF_4 (1.00 g/chamber, 0.3 M), CH_2Cl_2/H_3CCO_2H (10 mL/chamber, 9:1 v/v), carbon fibre electrodes, H-type cell, various currents, room temperature.
[b] Yields were determined by ^1H NMR analysis using mesitylene as internal standard.
[c] Isolated yield on a 2.0 g scale reaction.
[d] ce: current efficiency.

It also is mentionable that in all oxidative coupling reactions for product **7a** and **7b** an over-oxidation toward the radical cations was observed by an instantaneous appearance of a dark green colouration of the reaction mixture when electrolysis was continued after complete conversion of the starting material. Also precipitation, which might prevent the products from over-oxidation did not take place in all cases for triphenylene and quaterphenylene products **7** and **9** prepared in this work (see Table 4 and Table 5). Only in the cases where hexabenzocoronenes **13** and **16** were obtained precipitation was observed (see Scheme 5 and Scheme 6). The reduction of the over-oxidised products is carried out during the aqueous work-up. Such a behaviour has been intensively discussed in the past for oxidative coupling reactions of arenes, for example, triphenylenes.[23]

Summarising the results described above, we conclude that the optimised conditions for the electrolysis are as follows: DDQ (5 mol%) as redox mediator, Bu_4NBF_4 as supporting electrolyte, dichloromethane as solvent, trifluoroacetic acid as additive, in an divided cell equipped with carbon fibre electrodes under constant current conditions applying 10 mA at room temperature without special precautions for the exclusion of air or moisture.

With these optimised conditions in hand, we focused our efforts toward the electrochemical oxidation of various terphenyl derivatives. The results of these electrochemical transformations are summarised in Table 4.

In accordance with the results of the optimisation of the tetramethoxytriphenylene derivative **7b**, the oxidative coupling of **6c** to generate 2,3,7,10-tetramethoxytriphenylene (**7c**) was achieved in very good yield and current efficiency (entry 1). In this context, it is worthy of mention that if there are no directing

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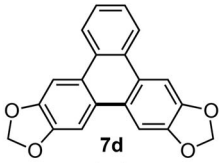
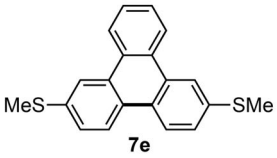
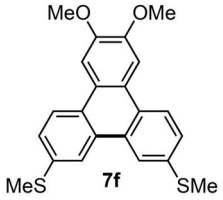
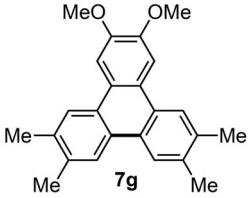
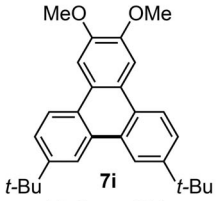
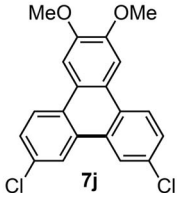
Table 4. Electrochemical oxidative coupling reaction of terphenyl derivatives under optimised reaction conditions.

Entry	Triphenylene **7c–j**	Yield[a] (ce)[b]
1	 **7c**	96% (91%)
2	 **7d**	73% (70%)
3	 **7e**	61% (60%)
4	 **7f**	67% (56%)
5	 **7g**	92% (88%)
6	 **7h**	93% (82%)
7	 **7i**	85% (77%)
8	 **7j**	82% (65%)

[a] *Reaction conditions:* terphenyl **6** (0.50 mmol, 1.0 equiv.), DDQ (5 mol%), Bu_4NBF_4 (0.3 M, 1.00 g/chamber), CH_2Cl_2/F_3CCO_2H (10 mL/chamber, 9:1 v/v), carbon fibre electrodes, 10 mA, room temperature, H-type cell.

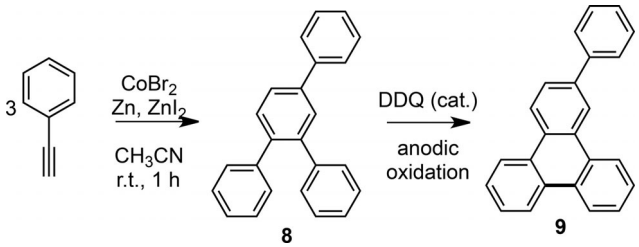
[b] ce: current efficiency.

groups in the 6- and 11-positions such as in **6a/6b** the 2- and 3-positions of the terphenyl have to be blocked by other substituents to achieve product formation. Otherwise, a complex mixture of several intramolecular coupling products will be observed. In contrast to **6b** by changing the veratryl fragments with benzo[1,3]dioxole moieties the oxidative coupling resulted in the formation of **7d** in a slightly decreased yield presumably due to a slow decomposition of the benzo[1,3]dioxole fragment of **6d** under acidic conditions (entry 2). This could also be proved by stirring **6d** in a mixture of dichloromethane and trifluoroacetic acid over 3 h followed by GC and GC-MS analysis.

Next, we turned our attention towards thioethers and alkyl-substituted substrates. The oxidative coupling of the methylthio-substituted terphenyl derivatives **6e/f** gave the desired products **7e/f** in 61% and 67% yield which are considerably lower than its methoxylated counterparts **7a/c** (entries 3 and 4). During these reactions, the formation of several unidentified side products was observed. However, the alkylated terphenyl derivatives **6g–i** gave the product in very good yields and current efficiencies (entries 5–7). In those cases, side products were not encountered, so that the terphenylene products could be obtained by simple filtration over a small pad of silica in pure form. Last, the oxidative coupling of **6j** provided the chlorinated triphenylene derivative **7j** in good yield but lower current efficiency (entry 8).

In a second set of experiments, we were interested to investigate the limits of this reaction. Therefore, we extended the aromatic system towards quaterphenyl derivatives **9** and hexaphenylbenzenes (HPB) **10/14**. Only few examples for oxidative coupling of quaterphenyls **9** have been reported thus far and a complex relationship between the substitution pattern and the applied oxidising agent was found.[24] In this context, we generated a number of 1,2,4-triphenylbenzene derivatives **8** by a cobalt-catalysed cyclotrimerisation of aryl-substituted alkynes to access the desired intermediates for further oxidation (Scheme 3).

The anodic oxidation of these derivatives was then investigated under the optimised conditions to afford



Scheme 3. Cobalt-catalysed synthesis of quaterphenyl and DDQ-catalysed anodic oxidation.

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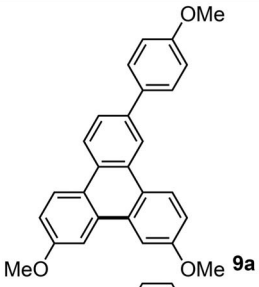
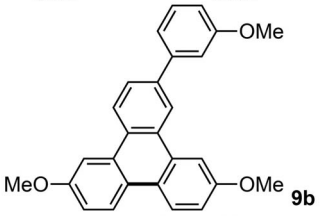
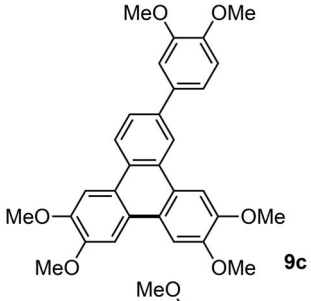
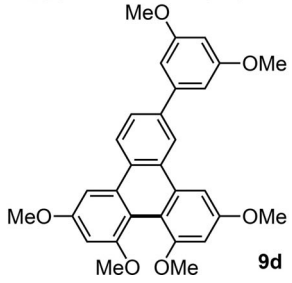
Table 5. Electrochemical oxidative coupling reaction of quaterphenyl derivatives for the synthesis of products of type **9**.

Entry	Quaterphenylene **9a–d**	Yield[a] (ce)[b]
1	 **9a**	79% (77%)
2	 **9b**	82% (70%)
3	 **9c**	90% (86%)
4	 **9d**	50% (21%)

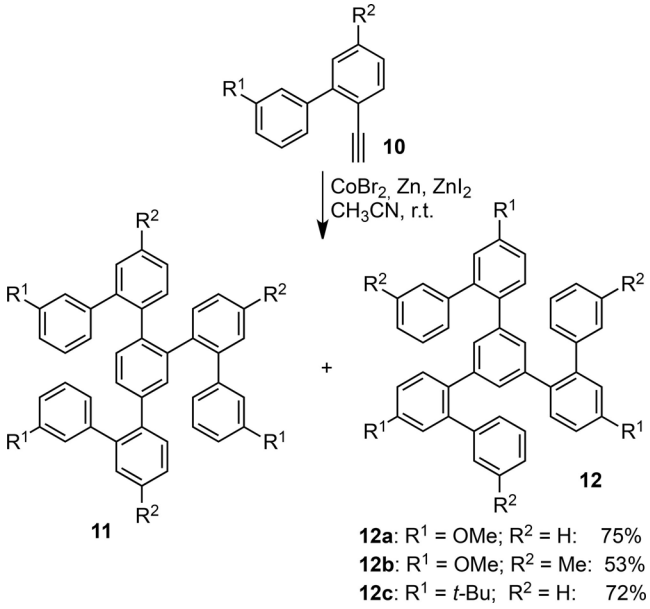
[a] *Reaction conditions:* quaterphenyl **8** (0.50 mmol, 1.0 equiv.), DDQ (5 mol%), Bu_4NBF_4 (0.3 M, 1.00 g/chamber), CH_2Cl_2/F_3CCO_2H (10 mL/chamber, 9:1 v/v), carbon fibre electrodes, 10 mA, room temperature, H-type cell.

[b] ce: current efficiency.

aryl-substituted triphenylenes of type **9**. The results are summarised in Table 5.

Methoxylated quaterphenyl derivatives **9a–c** underwent the transformation to aryl-substituted triphenylenes in very good yields and current efficiencies (Table 5, entries 1–3). Also, no intermolecular carbon-carbon bond formation with the additional phenyl ring was observed. Merely derivative **9d** was formed in moderate yield and rather long reaction time, presumably due to a steric hindrance of the methoxy groups at the triphenylene core (entry 4). Unfortunately, it was not possible to couple alkylated substrates with the terphenyl derivatives **6**. Nevertheless, the DDQ-mediated electrochemical oxidation could be performed successfully.

Next, we decided to enlarge the scope of oligophenylenes towards unsymmetrical starting materials, such as the trisbiphenylbenzene derivatives of type **11** (Scheme 4). These materials were obtained by palladium-catalysed cross-coupling of R^1-substituted areneboronic acids with R^2-substituted bromobenzaldehydes followed by a Corey–Fuchs reaction to convert the aldehyde into the terminal alkyne (see below for experimental details).



Scheme 4. Cobalt-catalysed cyclotrimerization for the synthesis of heptaphenylenes of type **11** or **12**.

As shown above, the cobalt-catalysed cyclotrimerisation of terminal alkynes led predominantly to 1,2,4-trisubstituted benzene derivatives. Similar results were obtained for the application of internal alkyl-aryl-substituted alkynes where the corresponding regioisomer was isolated. Accordingly, we expected that alkynyl-substituted biphenyl starting materials of type **10** would generate the corresponding 1,2,4-substituted products **11** (Scheme 4). From there unsymmetrical coronene derivatives were envisaged after indirect electrochemical oxidation.

However, we were surprised to identify the products derived from the cobalt-catalysed cyclotrimerisation reaction as the symmetrical 1,3,5-trisubstituted isomers of type **12** exclusively. Most likely, the steric bulkiness of the biaryl moieties forced the cyclotrimerisation to form the symmetrical product **12**. Accordingly, with the results of our previous work,[25] we have identified solvent, ligand as well as substrate ef-

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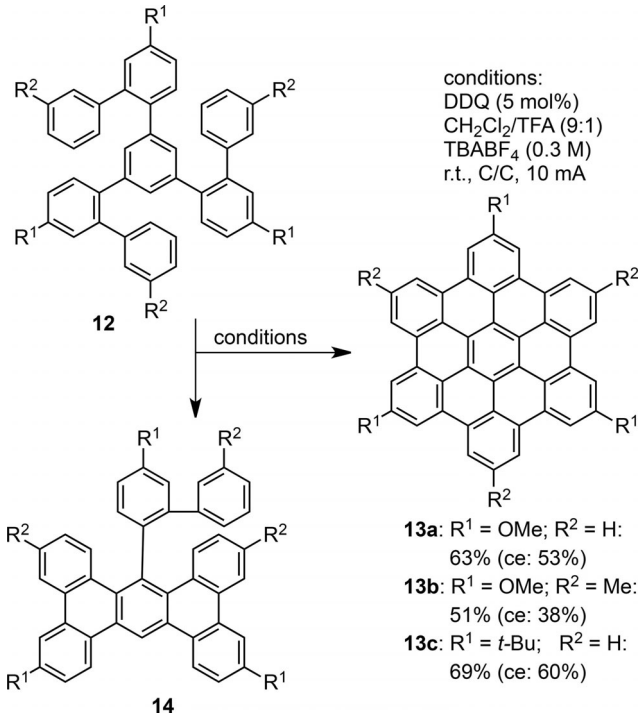
fects, described herein, of the cobalt-catalysed cyclotrimerisation reaction.

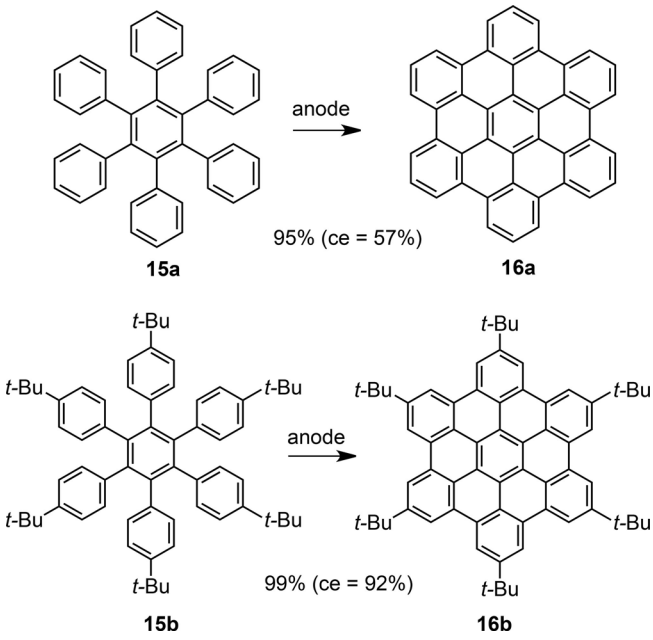
Even though the symmetrical product was formed, still two possible isomers could be formed upon an electrochemical DDQ-mediated oxidative coupling reaction (Scheme 5). For once, the planar coronene derivative **13** could be formed, but also the very interesting non-planar derivative **14** represents a possible isomer.[26] Therefore, we were very interested to see if a preference for one or the other product would be detectable under electrochemical conditions.



Scheme 5. Oxidative coupling of trisbiphenylbenzenes **12** under electrochemical conditions.

When the trisbiphenylbenzene derivatives of type **12** were subjected to the optimised conditions of the electrochemical DDQ-mediated oxidative coupling, only the coronene products **13** were isolated in acceptable chemical yields and current efficiencies (Scheme 5). Unfortunately, under the indirect electrochemical conditions no traces of products of type **14** were detected but also no other side products could be isolated. At this point we cannot exclude that those products **14** might be formed and lost during recrystallisation as well as column chromatography.

Finally, we turned our attention towards the application of hexaphenylbenzenes **15a** and **15b** as starting materials. Since these substrates have been reported numerous times in the literature, we only selected two derivatives for our study (Scheme 6). In these cases the two coronenes **16a** and **16b** could be isolated in



Scheme 6. Oxidative coupling of hexaphenyl benzenes **15** under electrochemical conditions.

excellent yields and good to excellent current efficiencies of 57% and 92%, respectively. It is noteworthy that only starting material and product could be observed by TLC analysis when less than 12 F/mol electricity was applied during the electrolysis of **15b**. This indicates that the first C–C bond being formed is the slowest. Surprising is the formation of **16a** under the reaction conditions, which has been reported to be impossible by using a stoichiometric DDQ/H_3CSO_3H system. It is conceivable that a combined direct and indirect electrochemical oxidation took place, where the first bond was formed by direct oxidative coupling enabling a further indirect oxidation process.

Although the advantages of an indirect electrochemical carbon-carbon bond formation should be obvious, we would like to illustrate the positive effects by a simple comparison: For the formation of **16b**, the chemical DDQ oxidation on a one gram scale utilised 1.56 gram of DDQ, resulting in a corresponding amount of spent as well as unreacted DDQ which had to be separated from the desired product. In contrast, the indirect electrochemical DDQ-mediated oxidation utilised 13 milligrams of DDQ. The criticism of the need for a supporting electrolyte is absolutely understandable in this context. However, the separation from the supporting electrolyte is rather easy.

Conclusions

In conclusion, we have developed an electrochemical intramolecular coupling reaction of arenes applying indirect anodic oxidation. The electrochemical synthe-

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sis was performed under constant current conditions in a divided cell using a catalytic amount of DDQ as redox mediator and a mixture of CH_2Cl_2 as solvent and trifluoroacetic acid as additive. Following a detailed optimisation of the reaction conditions, several terphenyl and quaterphenyl derivatives derived from simple Suzuki cross-coupling reactions or cobalt-catalysed alkyne trimerizations have been applied in the reaction and the resulting triphenylene derivatives were obtained in good to very good yields and excellent current efficiencies. A great advantage of the described procedure is in the avoidance of using stoichiometric amounts or large excesses of oxidants, which simplifies the work-up and minimises side-reactions. This could be demonstrated by the synthesis of several hexabenzocoronenes from heptaphenylenes and hexaphenylbenzenes where six carbon-carbon bonds were formed efficiently using just a catalytic amount of DDQ instead of over-stoichiometric amounts. Consequently, the electrochemical DDQ-mediated oxidative coupling of polyaromatic compounds broadens the scope of the Scholl reaction and serves as a novel efficient straightforward and atom economical method for such transformations.

Experimental Section

General Methods

All reactions requiring water- or air-sensitive compounds were carried out in vacuum- and flame-dried flasks utilizing Schlenk techniques under an argon atmosphere. DCM was dried over P_4O_{10}, while CH_3CN was dried over molecular sieve (3 Å) and distilled under a nitrogen atmosphere. ZnI_2 was dried under vacuum at 150 °C prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, at room temperature utilizing pre-set pulse programs. The chemical shifts are given relative to tetramethylsilane as an internal standard. The solvent signal was used for calibration [^{1}H NMR δ ($CHCl_3$) = 7.26 ppm, ^{13}C NMR δ ($CHCl_3$) = 77.16 ppm]. Infrared spectra (IR) were recorded on a FT-IR spectrometer. The absorption bands are given in wave numbers (cm^{-1}). High resolution mass spectra (HR-MS) were recorded as electron ionisation spectra (EI/HR-MS) utilizing a quadrupole mass analyser at an energy of 70 eV or as electron spray ionisation (ESI/HR-MS) using an LTQ-FT system. HR-FD mass spectra were acquired with an AccuTOF GCv 4G (JEOL) Time of Flight (TOF) mass spectrometer. An internal or external standard was used for drift time correction. The LIFDI ion source and FD-emitters were purchased from Linden ChroMasSpec GmbH. The detected ion masses (m/z) are reported in u corresponding to the intensity of the signals as a percentage of the most intense signal. Cyclic voltammetry measurements were carried out on a BAS C3 Cell Strand and a BAS 100 Electrochemical Analyser using glassy carbon disk working electrodes (2.0 mm diameter) and platinum wire counter electrodes (0.5 mm diameter). Potentials were referred to a saturated Ag/AgCl (0.3 M NaCl or saturated KCl) reference electrode. The solution was purged with nitrogen before each measurement. Electrochemical reactions were carried out in undivided cells with external cooling/heating circuit or H-type cells. Electrolysis was performed using a Temna digital-control and programmable DC power supply (model: 72-10480, 0–30 V, 0–3 A). Carbon fibre electrode material was purchased from R&G Faserverbundwerkstoffe GmbH Germany (item description: Carbon roving PyrofilTM TR50S 6k/400 tex). Before use, the carbon fibres were bound together (850 mg material) and contacted with a platinum wire.

General Procedure for the Suzuki-Type Coupling for the Preparation of Terphenyl Derivatives 6

The aryl halide (1.0 equiv.) and the boronic acid (1.0–1.5 equiv./halide) were dissolved in degassed toluene and aqueous sodium carbonate solution (2.5 M, 1:1 v/v, 15–30 mL mmol^{-1}). Then $Pd(PPh_3)_2Cl_2$ (5 mol%) was added and the reaction mixture was refluxed until complete conversion was determined by GC-MS analysis (14–20 h). After complete conversion, the mixture was cooled to room temperature, the organic phase was separated and the aqueous phase was extracted with diethyl ether (3 × 15 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (*n*-pentane/Et_2O) or by recrystallisation.

3,3″-Dimethoxy-1,1′:2′,1″-terphenyl (6a):[3c] Recrystallisation from ethanol (13 mL); white solid; yield: 2.22 g (7.65 mmol, 77%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.40 (m, 4H), 7.16 (t, J = 7.9 Hz, 2H), 6.83–6.74 (m, 4H), 6.70 (dd, J = 2.6, 1.6 Hz, 2H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 143.1, 140.6, 130.5, 129.0, 127.7, 122.4, 115.3, 112.8, 55.3.

3,3″,4,4″-Tetramethoxy-1,1′:2′,1″-terphenyl (6b):[3d] Recrystallisation from ethanol (74 mL); white solid; yield: 6.24 g (17.8 mmol, 89%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.35 (m, 4H), 6.78 (d, J = 1.1 Hz, 4H), 6.62 (t, J = 1.2 Hz, 2H), 3.86 (s, 6H), 3.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 148.0, 140.4, 134.6, 130.5, 127.4, 122.0, 113.8, 111.1, 56.1, 55.9.

4,4′,4″,5′-Tetramethoxy-1,1′:2′,1″-terphenyl (6c): Recrystallisation from ethanol (25 mL); white solid; yield: 915 mg (2.61 mmol, 87%); mp 140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12–7.02 (m, 4H), 6.90 (s, 2H), 6.83–6.72 (m, 4H), 3.93 (s, 6H), 3.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 148.2, 134.2, 132.7, 131.1, 113.9, 113.6, 56.2, 55.3; IR (ATR): ν = 3000, 2956, 2836, 1604, 1495, 1461, 1440, 1234, 1170, 1110, 1024, 915, 871, 830, 808, 781, 617, 537; MS (EI$^+$): m/z = 350 (100, [M]$^+$), 335 (10), 307 (25), 292 (3), 261 (5), 233 (3), 189 (5), 152 (4), 132 (7), 89 (2); HR-MS (EI$^+$): m/z = 350.1510, calculated for $C_{22}H_{22}O_4$ ([M]$^+$): 350.1518.

1,2-Bis(benzo[*d*][1,3]dioxol-5-yl)benzene (6d): Recrystallisation from ethanol (25 mL); white solid; yield: 688 mg (2.16 mmol, 72%); mp 125–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (s, 4H), 6.71 (d, J = 8.4 Hz, 2H), 6.67–6.58 (m, 4H), 5.93 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.4, 146.4, 140.3, 135.7, 130.7, 127.4, 123.4, 110.4, 108.1, 101.0; IR (ATR): ν = 2956, 2904, 2868, 1602, 1497, 1459, 1384, 1353, 1262, 1235, 1201, 1160, 1114, 1028, 918, 869, 832, 795, 738, 654, 568; MS (EI$^+$): m/z = 318 (100, [M]$^+$), 287 (8),

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259 (15), 231 (6), 202 (23), 189 (4), 158 (7), 129 (4), 101 (15), 75 (2); HR-MS (EI$^+$): m/z = 318.0891, calculated for $C_{20}H_{14}O_4$ ([M]$^+$): 318.0892.

3,3″-Bis(methylthio)-1,1′:2′,1″-terphenyl (6e): Flash chromatography (eluent: *n*-pentane/diethyl ether 50:1); white solid; yield: 1.38 g (4.29 mmol, 81%); mp 69–71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.41 (m, 4H), 7.20–7.09 (m, 4H), 7.04–6.91 (m, 4H), 2.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.2, 140.2, 138.2, 130.5, 128.5, 128.4, 127.9, 126.8, 125.4, 16.0; IR (ATR): ν = 3054, 2976, 2917, 2863, 1585, 1562, 1462, 1433, 1396, 1262, 1165, 1093, 1026, 960, 878, 788, 754, 695; MS (EI$^+$): m/z = 322 (100, [M]$^+$), 274 (24), 260 (17), 259 (24), 228 (46); HR-MS (EI$^+$): m/z = 322.0850, calculated for $C_{20}H_{18}S_2$ ([M]$^+$): 322.0850.

(4′,5′-Dimethoxy-[1,1′:2′,1″-terphenyl]-4,4″-diyl)bis(methylsulfane) (6f): Recrystallisation from ethanol (21 mL); white solid; yield: 681 mg (1.78 mmol, 89%); mp 135–137 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (q, J = 8.5 Hz, 8H), 6.90 (s, 2H), 3.93 (s, 6H), 2.47 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 138.4, 136.6, 132.5, 130.5, 126.3, 113.9, 56.2, 15.9; IR (ATR): ν = 2963, 2920, 2839, 1598, 1546, 1516, 1483, 1441, 1384, 1347, 1259, 1232, 1204, 1160, 1095, 961, 862, 824, 793, 735, 638; MS (EI$^+$): m/z = 382 (100, [M]$^+$), 367 (6), 339 (17), 320 (3), 292 (13), 245 (7), 202 (9), 148 (10), 105 (11), 77 (9); HR-MS (EI$^+$): m/z = 382.1062, calculated for $C_{22}H_{22}O_2S_2$ ([M]$^+$): 382.1061.

4′,5′-Dimethoxy-3,3″,4,4″-tetramethyl-1,1′:2′,1″-terphenyl (6g): Recrystallisation from ethanol (16 mL); white solid; yield: 631 mg (1.82 mmol, 91%); mp 105–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (d, J = 2.0 Hz, 2H), 6.98–6.90 (m, 4H), 6.82 (dd, J = 7.8, 2.0 Hz, 2H), 3.94 (s, 6H), 2.23 (s, 6H), 2.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9, 139.1, 135.9, 134.3, 133.0, 130.9, 129.0, 127.4, 113.8, 56.0, 19.7, 19.3; IR (ATR): ν = 3003, 2913, 2837, 1601, 1493, 1445, 1867, 1338, 1237, 1203, 1177, 1146, 1031, 859, 813, 774, 583; MS (EI$^+$): m/z = 346 (100, [M]$^+$), 331 (5), 303 (19), 288 (2), 273 (12), 259 (4), 245 (7), 230 (8), 215 (5), 197 (2), 173 (2), 158 (4), 115 (3); HR-MS (EI$^+$): m/z = 346.1921, calculated for $C_{24}H_{26}O_2$ ([M]$^+$): 346.1933.

3,3″-Di-*tert*-butyl-4′,5′-dimethoxy-1,1′:2′,1″-terphenyl (6h): Recrystallisation from ethanol (15 mL); white solid; yield: 773 mg (1.92 mmol, 96%); mp 82–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.08 (m, 6H), 7.03–6.96 (m, 4H), 3.96 (s, 6H), 1.09 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.6, 148.3, 141.2, 134.0, 128.3, 127.9, 126.6, 123.1, 113.8, 56.3, 34.5, 31.3; IR (ATR): ν = 3056, 2956, 2905, 2868, 2838, 1601, 1515, 1475, 1457, 1414, 1386, 1350, 1321, 1252, 1234, 1206, 1165, 1030, 860, 795, 754, 708, 602; MS (EI$^+$): m/z = 402 (100, [M]$^+$), 387 (4), 359 (4), 331 (7), 319 (22), 301 (4), 270 (10), 241 (3), 207 (5), 165 (2), 128 (2), 91 (7), 67 (2), 57 (29); HR-MS (EI$^+$): m/z = 402.2559, calculated for $C_{28}H_{34}O_2$ ([M]$^+$): 402.2559.

4,4″-Di-*tert*-butyl-4′,5′-dimethoxy-1,1′:2′,1″-terphenyl (6i): Recrystallisation from ethanol (15 mL); white solid; yield: 1.14 g (2.81 mmol, 94%);: mp 120–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.18 (m, 4H), 7.11–7.03 (m, 4H), 6.95 (s, 2H), 3.94 (s, 6H), 1.31 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2, 148.2, 138.7, 133.2, 129.7, 124.8, 114.0, 56.2, 34.5, 31.5; IR (ATR): ν = 2956, 2904, 2868, 1602, 1497, 1459, 1384, 1353, 1262, 1235, 1201, 1160, 1114, 1028, 918, 869, 832, 795, 738, 654, 568; MS (EI$^+$): m/z = 402 (100, [M]$^+$), 387 (56), 359 (1), 316 (12), 274 (2), 241 (2), 215 (3), 186 (11), 158 (9), 115 (3), 59 (23); HR-MS (EI$^+$): m/z = 402.2555, calculated for $C_{28}H_{34}O_2$ ([M]$^+$): 402.2559.

4,4″-Dichloro-4′,5′-dimethoxy-1,1′:2′,1″-terphenyl (6j): Flash chromatography (eluent: *n*-pentane/diethyl ether 5:1); white solid; yield: 677 mg (1.86 mmol, 93%); mp 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.16 (m, 4H), 7.09–7.00 (m, 4H), 6.88 (s, 2H), 3.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 139.8, 132.7, 132.0, 131.3, 128.4, 113.8, 56.3; IR (ATR): ν = 2991, 2959, 2931, 2904, 2835, 1599, 1519, 1483, 1459, 1347, 1246, 1203, 1163, 1086, 1029, 869, 827, 731, 700; MS (EI$^+$): m/z = 358 (100, [M]$^+$), 343 (10), 315 (22), 265 (13), 215 (6), 202 (24), 189 (2), 162 (4), 136 (16), 125 (3), 100 (7), 75 (4); HR-MS (EI$^+$): m/z = 358.0521, calculated for $C_{20}H_{16}Cl_2O_2$ ([M]$^+$): 358.0527.

General Procedure for the Suzuki-Type Coupling for the Synthesis of 1,1′-Biphenyl-2-carbaldehydes

$Pd(PPh_3)_2Cl_2$ (5 mol%) and sodium carbonate (2.0 equiv.) were dissolved in a degassed mixture of toluene/water/ethanol (6:3:1 v/v/v). The 2-bromobenzaldehyde (1.0 equiv.) and the boronic acid (1.2 equiv.) were added and the reaction mixture was refluxed for until complete conversion was determined by GC-MS and TLC analysis (5–6 h). The mixture was cooled to room temperature, diethyl ether (10 mL) was added, the organic phase was separated and the aqueous phase was extracted with diethyl ether (3x 15 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography.

3′-Methoxy-[1,1′-biphenyl]-2-carbaldehyde:[27] Flash chromatography (eluent: *n*-pentane/diethyl ether 10:1); colourless oil; yield: 2.06 g (9.70 mmol, 97%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.02 (dd, J = 7.8, 1.5 Hz, 1H), 7.63 (td, J = 7.5, 1.5 Hz, 1H), 7.55–7.42 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.03–6.89 (m, 3H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.5, 159.7, 146.0, 139.3, 134.0, 133.6, 130.7, 129.6, 128.0, 127.6, 122.9, 115.8, 113.8, 55.5.

3′-Methoxy-5-methyl-[1,1′-biphenyl]-2-carbaldehyde: Flash chromatography (eluent: *n*-pentane/diethyl ether 15:1→10:1→5:1); colourless oil; yield: 1.07 g (4.72 mmol, 94%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.95 (d, J = 0.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.25 (d, J = 1.6 Hz, 1H), 7.01–6.89 (m, 3H), 3.86 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.2, 159.7, 146.1, 144.6, 139.5, 131.7, 131.3, 129.5, 128.9, 127.7, 122.8, 115.8, 113.7, 55.5, 21.9; IR (ATR): ν = 3002, 2944, 2841, 2753, 1685, 1598, 1481, 1457, 1428, 1397, 1282, 1265, 1220, 1165, 1119, 1033, 874, 824, 785, 700; MS (EI$^+$): m/z = 226 (100, [M]$^+$), 211 (17), 198 (79), 183 (9), 167 (29), 155 (30), 128 (11), 89 (5), 63 (7); HR-MS (EI$^+$): m/z = 226.0990, calculated for $C_{15}H_{14}O_2$ ([M]$^+$): 226.0994.

3′-(*tert*Butyl)-[1,1′-biphenyl]-2-carbaldehyde: Flash chromatography (eluent: *n*-pentane/diethyl ether 50:1→25:1); colourless oil; yield: 1.14 g (4.78 mmol, 91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (d, J = 0.8 Hz, 1H), 8.10–7.99 (m, 1H), 7.65 (td, J = 7.5, 1.5 Hz, 1H), 7.55–7.45 (m, 3H), 7.45–7.34 (m, 2H), 7.21 (dt, J = 7.4, 1.5 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.7, 151.6, 146.7, 137.6, 134.0, 133.6, 130.9, 128.3, 127.8, 127.6, 127.5, 127.3, 125.2, 34.9, 31.5; IR (ATR): ν = 3062, 2960, 2905, 2867, 2751, 1690, 1596, 1472, 1393, 1364, 1265, 1245, 1194, 826, 801, 762,

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708, 627; MS (EI$^+$): m/z = 238 (66, [M]$^+$), 223 (100), 205 (58), 195 (20), 181 (57), 165 (37), 152 (28), 139 (4), 104 (9), 77 (7), 57 (10); HR-MS (EI$^+$): m/z = 238.1358, calculated for $C_{17}H_{18}O$ ([M]$^+$): 238.1358.

General Procedure for the Corey–Fuchs Reaction

PPh_3 (3.6 equiv.) was dissolved in dichloromethane (3 mL mmol^{-1}), CBr_4 (1.8 equiv.) was added slowly at 0 °C and the solution was stirred for 15 min. Then, the [1,1′-biphenyl]-2-carbaldehyde (1.0 equiv.) was added and the mixture was stirred for 2 h at room temperature. The mixture was concentrated, *n*-pentane (2 mL mmol^{-1}) was added, the mixture was filtered over a plug of silica (eluent: *n*-pentane/dichloromethane 5:1) and the solvent was removed under reduced pressure. The resulting dibromo-olefin was dissolved in tetrahydrofuran (1 mL mmol^{-1}), the mixture was cooled to −35 °C and *n*-BuLi (2.5 M in hexane, 2.2 equiv.) was added. The mixture was allowed to warm up to room temperature and was stirred until completion was determined by GC-MS and TLC analysis (2 h). It was quenched with saturated aqueous NH_4Cl solution, the organic phase was separated and washed with brine (3 × 15 mL) and the aqueous phase was extracted with diethyl ether (3 × 15 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography.

2-Ethynyl-3′-methoxy-1,1′-biphenyl (10a):[28] Flash chromatography (eluent: *n*-pentane/diethyl ether 10:1→7:1); colourless oil; yield: 1.47 g (7.07 mmol, 75%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (dt, J = 7.6, 1.1 Hz, 1H), 7.49–7.27 (m, 4H), 7.25–7.18 (m, 2H), 6.97 (ddd, J = 8.2, 2.5, 1.1 Hz, 1H), 3.90 (s, 3H), 3.11 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 144.4, 141.8, 134.1, 129.7, 129.1, 129.1, 127.2, 121.8, 120.6, 115.0, 113.5, 83.3, 80.4, 55.4.

2-Ethynyl-3′-methoxy-5-methyl-1,1′-biphenyl (10b): Flash chromatography (eluent: *n*-pentane/diethyl ether 7:1→5:1); white solid; yield: 1.28 g (5.76 mmol, 65%); mp 55–58 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 8.1 Hz, 1H), 7.24–7.08 (m, 4H), 6.93 (ddd, J = 8.3, 2.6, 1.1 Hz, 1H), 3.86 (s, 3H), 3.03 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 144.3, 141.9, 139.2, 134.0, 130.4, 129.1, 128.0, 121.8, 117.6, 114.9, 113.5, 83.4, 79.7, 55.4, 21.6; IR (ATR): ν = 3272, 3034, 2999, 2966, 2933, 2836, 1603, 1574, 1462, 1431, 1218, 1166, 1031, 870, 828, 783, 696, 656, 622, 543, 508; MS (EI$^+$): m/z = 222 (100, [M]$^+$), 207 (40), 179 (78), 152 (12), 111 (3), 89 (3), 63 (2); HR-MS (EI$^+$): m/z = 222.1033, calculated for $C_{16}H_{14}O$ ([M]$^+$): 222.1045.

3′-(*tert*Butyl)-2-ethynyl-1,1′-biphenyl (10c): Flash chromatography (eluent: *n*-pentane/diethyl ether 50:1); red oil; yield: 906 mg (3.87 mmol, 92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (q, J = 1.4 Hz, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.50–7.34 (m, 5H), 7.31 (dq, J = 8.7, 4.1 Hz, 1H), 3.04 (s, 1H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.7, 145.1, 139.9, 134.1, 129.8, 129.1, 127.9, 127.1, 127.0, 126.3, 124.5, 120.6, 83.6, 80.1, 35.0, 31.5; IR (ATR): ν = 3287, 3061, 2959, 2868, 1598, 1471, 1409, 1363, 1241, 1205, 1098, 965, 798, 757, 705, 635, 611; MS (EI$^+$): m/z = 234 (8, [M]$^+$), 219 (30), 202 (15), 189 (7), 179 (41), 165 (5), 150 (3), 109 (2), 101 (5), 95 (5), 82 (7), 57 (33); HR-MS (EI$^+$): m/z = 234.1420, calculated for $C_{18}H_{18}$ ([M]$^+$): 234.1409.

General Procedure for the Cobalt-Catalysed Cyclotrimerisation of Alkynes

Under an argon atmosphere cobalt(II) bromide (10 mol%), zinc powder (10 mol%) and anhydrous zinc iodide (10 mol%) were dissolved in acetonitrile (2 mL mmol^{-1}). The alkyne (1.0 equiv.) was added and the reaction mixture was stirred at ambient temperature until complete conversion was determined by TLC analysis (1 h). After complete reaction *n*-pentane was added followed by filtration over a plug of silica (eluent: *n*-pentane/diethyl ether) and the solvent was removed. The crude product was suspended in ethanol (1 mL mmol^{-1}) and heated to reflux. More ethanol was added until the remaining solid had dissolved completely. Then, water was added until precipitation was observed and the mixture was cooled over 16 h. The solid was filtered off and dried under reduced pressure to give the product.

4,4″-Dimethoxy-4′-(4-methoxyphenyl)-1,1′:2′,1″-terphenyl (8a):[24b] Recrystallisation from ethanol/water (23 mL, 2:1 v/v); yellow solid; yield: 456 mg (1.15 mmol, 87%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.55 (m, 4H), 7.45 (dd, J = 7.8, 0.7 Hz, 1H), 7.20–7.06 (m, 4H), 7.08–6.95 (m, 2H), 6.80 (dq, J = 8.4, 3.0 Hz, 4H), 3.87 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 158.5, 158.4, 140.6, 139.8, 138.6, 134.3, 133.9, 133.4, 131.15, 131.11, 131.0, 129.1, 128.2, 125.5, 114.4, 113.6, 113.6, 55.5, 55.32, 55.26.

3,3″-Dimethoxy-4′-(3-methoxyphenyl)-1,1′:2′,1″-terphenyl (8b): Flash chromatography (eluent: *n*-pentane/diethyl ether 5:1); yellow oil; yield: 1.46 g (3.68 mmol, 91%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.63 (m, 2H), 7.53 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.32–7.14 (m, 4H), 6.94 (dd, J = 8.2, 2.5 Hz, 1H), 6.87–6.72 (m, 6H), 3.89 (s, 3H), 3.65 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2, 159.4, 159.3, 143.0, 142.6, 142.3, 141.0, 140.5, 139.8, 131.0, 130.0, 129.4, 129.10, 129.07, 126.4, 122.5, 122.4, 119.8, 115.4, 115.3, 113.1, 113.0, 112.98, 112.9, 55.5, 55.29, 55.27; IR (ATR): ν = 2999, 2939, 2836, 1582, 1518, 1485, 1448, 1243, 1212, 1134, 1020, 867, 809, 761; MS (EI$^+$): m/z = 396 (100, [M]$^+$), 365 (10), 333 (7), 278 (5), 198 (5), 144 (3), 91 (5); HR-MS (EI$^+$): m/z = 396.1727, calculated for $C_{27}H_{24}O_3$ ([M]$^+$): 396.1725.

4′-(3,4-Dimethoxyphenyl)-3,3″,4,4″-tetramethoxy-1,1′:2′,1″-terphenyl (8c):[24a] Recrystallisation from ethanol (17 mL); yellow solid; yield: 596 mg (1.23 mmol, 78%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.47 (m, 2H), 7.42 (d, J = 7.9 Hz, 1H), 7.17–7.07 (m, 2H), 6.89 (d, J = 8.3 Hz, 1H), 6.81–6.67 (m, 4H), 6.58 (dd, J = 9.6, 1.7 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.55 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.5, 149.0, 148.6, 148.5, 148.1, 148.0, 140.7, 140.2, 139.0, 134.6, 134.2, 133.8, 130.9, 128.9, 125.8, 122.0, 122.0, 119.6, 113.8, 113.7, 111.8, 111.12, 111.09, 110.7, 56.2 (2C), 56.1, 56.0, 55.9, 55.8.

4′-(3,5-Dimethoxyphenyl)-3,3″,5,5″-tetramethoxy-1,1′:2′,1″-terphenyl (8d): Recrystallisation from ethanol (24 mL); yellow solid; yield: 753 mg (1.55 mmol, 75%); mp 167–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 1.9 Hz, 1H), 7.63 (dd, J = 7.9, 2.0 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 6.81 (d, J = 2.3 Hz, 2H), 6.50 (t, J = 2.2 Hz, 1H), 6.41 (d, J = 2.3 Hz, 2H), 6.39 (d, J = 2.2 Hz, 2H), 6.35 (dt, J = 4.4, 2.3 Hz, 2H), 3.86 (s, 6H), 3.65 (s, 6H), 3.65 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (2C), 160.50 (2C), 160.45 (2C), 143.6, 143.2, 142.9, 141.0, 140.7, 139.9,

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130.8, 129.1, 126.4, 108.1 (2C), 108.0 (2C), 105.6 (2C), 99.8, 99.52, 99.46, 55.6 (2C), 55.49 (2C), 55.46 (2C); IR (ATR): ν=3009, 2937, 2837, 1591, 1456, 1422, 1332, 1199, 1046, 1031, 935, 860, 830, 699, 568; MS (EI$^+$): m/z=486 (100, [M]$^+$), 471 (7), 455 (7), 364 (9), 243 (7), 191 (2), 84 (17); HR-MS (EI$^+$): m/z=486.2045, calculated for $C_{30}H_{30}O_6$ ([M]$^+$): 486.2042.

5″-([3′-Methoxy-1,1′-biphenyl]-2-yl)-1,1′:2′,1″:3″,1‴:2‴,1⁗-quinquephenyl (12a): Recrystallisation from ethanol (31 mL); dark red solid; yield: 756 mg (1.21 mmol, 75%); mp 208–210 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.33–7.22 (m, 6H), 7.18 (td, J=7.1, 1.8 Hz, 3H), 7.11 (t, J=7.9 Hz, 3H), 6.75 (s, 3H), 6.72 (s, 6H), 6.66 (s, 3H), 6.49 (d, J=7.6 Hz, 3H), 3.62 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.5, 143.2, 140.8, 140.50, 140.45, 130.6, 130.3, 129.8, 129.0, 127.5, 127.4, 123.1, 115.8, 112.3, 55.4; IR (ATR): ν=3052, 2937, 2831, 1582, 1470, 1416, 1294, 1263, 1294, 1263, 1209, 1167, 1046, 1017, 881, 858, 755, 697, 617; MS (EI$^+$): m/z=624 (100, [M]$^+$), 592 (1), 486 (31), 427 (6), 363 (3), 312 (1), 243 (2), 195 (9), 130 (2), 68 (4); HR-MS (EI$^+$): m/z=624.2668, calculated for $C_{45}H_{36}O_3$ ([M]$^+$): 624.2664.

5″-([3′-Methoxy-4-methyl-1,1′-biphenyl]-2-yl)-1,1′:2′,1″:3″,1‴:2‴,1⁗-quinquephenyl (12b): Recrystallisation from ethanol (45 mL); dark red solid; yield: 533 mg (0.80 mmol, 53%); mp 232–234 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.17 (s, 3H), 7.14–7.07 (m, 5H), 6.99 (dd, J=7.9, 1.8 Hz, 3H), 6.82 (t, J=8.0 Hz, 2H), 6.78–6.68 (m, 4H), 6.68–6.63 (m, 5H), 6.53–6.44 (m, 2H), 3.61 (s, 9H), 2.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.4, 143.2, 140.5, 140.2, 137.7, 136.9, 130.9, 130.4, 129.5, 128.8, 128.1, 122.9, 115.5, 112.1, 55.2, 21.0; IR (ATR): ν=2999, 2918, 2832, 1598, 1579, 1475, 1458, 1426, 1312, 1282, 1260, 1221, 1167, 1038, 877, 816, 783, 697; MS (EI$^+$): m/z=666 (34, [M]$^+$), 486 (100), 471 (7), 222 (58), 207 (22), 178 (21), 152 (8), 131 (12), 105 (11), 91 (13), 68 (20); HR-MS (EI$^+$): m/z=666.3121, calculated for $C_{48}H_{42}O_3$ ([M]$^+$): 666.3134.

5″-([3′-(*tert*-Butyl)-1,1′-biphenyl]-2-yl)-1,1′:2′,1″:3″,1‴:2‴,1⁗-quinquephenyl (12c): Recrystallisation from ethanol (14 mL); yellow solid; yield: 584 mg (0.83 mmol, 71%); mp 178–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40 (s, 3H), 7.33 (td, J=6.7, 5.8, 1.5 Hz, 3H), 7.29–7.27 (m, 2H), 7.25 (dd, J=2.2, 1.2 Hz, 2H), 7.23 (d, J=2.6 Hz, 2H), 7.19 (dq, J=4.4, 1.4 Hz, 4H), 7.17–7.10 (m, 4H), 6.79–6.58 (m, 7H), 1.19 (s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=150.9, 141.5, 141.1, 140.4, 140.2, 130.2, 130.1, 129.8, 127.5, 127.4, 127.3, 127.1, 127.0, 123.2, 34.6, 31.3; IR (ATR): ν=3057, 2958, 2867, 1595, 1473, 1407, 1362, 1259, 1091, 1021, 895, 866, 797, 753, 706; MS (EI$^+$): m/z=703 (100, [M]$^+$), 645 (57), 568 (19), 493 (21), 473 (11), 305 (5), 209 (15), 133 (19); HR-MS (EI$^+$): m/z=703.4220, calculated for $C_{54}H_{54}$ ([M]$^+$): 703.4226.

General Procedure for the Electrochemical DDQ-Mediated Oxidative Coupling

In an H-type cell the anodic chamber was charged with substrate (1.0 equiv.) and DDQ (5 mol%). In addition, both chambers were charged with $TBABF_4$ (0.3 M, 1.00 g/chamber) and dichloromethane/trifluoroacetic acid (10 mL/chamber, 9:1 v/v). The cell was equipped with carbon fibre electrodes and electrolysed at room temperature under constant current (10 mA). The reaction progress was monitored by TLC and GC-MS analysis. After complete conversion the solution was diluted with dichloromethane (15–30 mL) and the organic phase was neutralised with aqueous ammonia solution (20 mL, 5 M) (the electrodes should be rinsed thoroughly) and the organic phase was separated. The aqueous phase was extracted (3×10 mL) and the combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (*n*-pentane/diethyl ether) or by recrystallisation.

2,7-Dimethoxytriphenylene (7a):[22] Flash chromatography (eluent: *n*-pentane/diethyl ether 3:1→1:1); white solid; yield: 97 mg (0.43 mmol, 85%, 2.05 F, 82% ce); ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.61–8.51 (m, 2H), 8.42 (d, J=9.0 Hz, 2H), 8.01 (d, J=2.7 Hz, 2H), 7.73–7.57 (m, 2H), 7.24 (dd, J=9.0, 2.6 Hz, 2H), 4.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.4, 130.3, 130.1, 127.2, 124.5, 124.1, 123.5, 116.0, 106.0, 55.6.

2,3,6,7-Tetramethoxytriphenylene (7b):[3d] Flash chromatography (eluent: dichloromethane/methanol 3:1→1:1); white solid; yield: 160 mg (0.46 mmol, 92%, 2.01 F, 91% ce); ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.44 (dt, J=7.4, 3.6 Hz, 2H), 7.91 (s, 2H), 7.67 (s, 2H), 7.59 (ddd, J=6.3, 3.3, 1.0 Hz, 2H), 4.10 (br s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=149.5, 149.0, 129.0, 126.1, 124.0, 123.6, 122.9, 104.8, 104.4, 56.2, 56.1.

2,3,7,10-Tetramethoxytriphenylene (7c): Flash chromatography (eluent: *n*-pentane/diethyl ether 1:1); white solid; yield: 168 mg (0.48 mmol, 96%, 2.11 F, 91% ce); mp 157–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.35 (d, J=9.0 Hz, 2H), 7.92 (d, J=2.6 Hz, 2H), 7.82 (s, 2H), 7.25 (dd, J=9.0, 2.5 Hz, 2H), 4.09 (s, 6H), 4.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.2, 149.0, 130.3, 124.5, 124.2, 123.3, 115.8, 106.2, 104.4, 56.1, 55.6; IR (ATR): ν=3097, 2995, 2927, 2833, 2065, 1612, 1505, 1452, 1417, 1346, 1306, 1259, 1205, 1162, 1045, 1021, 924, 831, 796, 574, 537; MS (EI$^+$): m/z=348 (100, [M]$^+$), 333 (20), 318 (2), 305 (22), 290 (12), 274 (5), 262 (8), 247 (8), 219 (7), 174 (12), 131 (5), 100 (2), 57 (1); HR-MS (EI$^+$): m/z=348.1372, calculated for $C_{22}H_{20}O_4$ ([M]$^+$): 348.1362.

Triphenyleno[2,3-*d*:6,7-*d*′]bis([1,3]dioxole) (7d): Flash chromatography (eluent: diethyl ether); pale yellow solid; yield: 115 mg (0.36 mmol, 73%, 2.01 F, 70% ce); mp 162–164 °C. The compound is too poorly soluble in organic solvents for NMR analysis. CHN analysis: ($C_{20}H_{12}O_4$, MW: 316.31 g mol^{-1}); found (calculated): C: 75.89% (75.94%), H: 3.75% (3.82%); IR (ATR): ν=2960, 2919, 1725, 1501, 1453, 1377, 1255, 1206, 1092, 1028, 935, 901, 852, 797, 749, 700, 618; MS (EI$^+$): m/z=316 (100, [M]$^+$), 293 (11), 258 (6), 228 (7), 200 (22), 149 (41), 127 (7), 100 (11), 71 (15), 69 (10), 57 (19); HR-MS (EI$^+$): m/z= calculated for $C_{20}H_{12}O_4$ ([M]$^+$): 316.0736; found: 316.0747.

2,7-Bis(methylthio)triphenylene (7e): Flash chromatography (eluent: *n*-pentane/diethyl ether 50:1→20:1→10:1); white solid; yield: 97 mg (0.30 mmol, 61%, 2.02 F, 60% ce); mp 164–165 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.58 (dd, J=6.2, 3.4 Hz, 2H), 8.45 (dd, J=5.4, 3.4 Hz, 4H), 7.65 (dd, J=6.3, 3.3 Hz, 2H), 7.53 (dd, J=8.5, 1.9 Hz, 2H), 2.67 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=137.5, 130.1, 129.6, 127.6, 127.3, 126.4, 123.7, 123.4, 121.1, 16.4; IR (ATR): ν=3054, 2960, 2920, 2854, 1726, 1591, 1432, 1399, 1258, 1091, 1018, 956, 868, 796, 757, 696, 586; MS (EI$^+$): m/z=320 (100,

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[M]$^+$), 305 (56), 274 (19), 258 (54), 246 (17), 231 (20), 226 (23), 149 (15), 97 (5), 71 (10), 57 (16); HR-MS (EI$^+$): m/z = 320.0712, calculated for $C_{20}H_{16}S_2$ ([M]$^+$): 320.0693.

(6,7-Dimethoxytriphenylene-2,11-diyl)bis(methylsulfane) (7f): Flash chromatography (eluent: *n*-pentane/diethyl ether 5:1→3:1); yellow solid; yield: 128 mg (0.34 mmol, 67%, 2.39 F, 56% ce); mp 172–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (d, J = 2.0 Hz, 2H), 8.25 (dd, J = 8.7, 4.1 Hz, 2H), 7.77 (s, 2H), 7.50–7.32 (m, 2H), 4.03 (d, J = 2.2 Hz, 6H), 2.59 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.6, 136.4, 129.1, 127.6, 126.6, 123.8, 123.5, 121.4, 104.5, 56.2, 16.6; IR (ATR): ν = 2560, 2917, 2855, 1601, 1533, 1496, 1440, 1402, 1261, 1199, 1159, 1091, 1017, 866, 837, 791, 587; MS (EI$^+$): m/z = 380 (100, [M]$^+$), 365 (16), 322 (6), 290 (23), 275 (6), 232 (4), 190 (10), 147 (6), 116 (3); HR-MS (EI$^+$): m/z = 380.0901, calculated for $C_{22}H_{20}O_2S_2$ ([M]$^+$): 380.0905.

2,3-Dimethoxy-6,7,10,11-tetramethyltriphenylene (7g): Flash chromatography (eluent: diethyl ether); yellow solid; yield: 158 mg (0.46 mmol, 92%, 2.10 F, 88% ce); mp 216–217 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 2H), 8.17 (s, 2H), 7.93 (s, 2H), 4.12 (s, 6H), 2.51 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1, 135.5, 135.1, 127.5, 127.4, 123.9, 123.8, 123.3, 104.6, 56.1, 20.40, 20.35; IR (ATR): ν = 2915, 2856, 1736, 1612, 1506, 1443, 1410, 1374, 1257, 1202, 1166, 1143, 1036, 848, 806, 645; MS (EI$^+$): m/z = 344 (2, [M]$^+$), 291 (3), 267 (2), 253 (1), 202 (100), 174 (23), 150 (39), 126 (14), 111 (10), 98 (15), 74 (4); HR-MS (EI$^+$): m/z = 344.1770, calculated for $C_{24}H_{24}O_2$ ([M]$^+$): 344.1776.

6,11-Di-*tert*-butyl-2,3-dimethoxytriphenylene (7h): Flash chromatography (eluent: diethyl ether); yellow solid; yield: 185 mg (0.46 mmol, 93%, 2.16 F, 82% ce); mp 157–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (d, J = 8.6 Hz, 2H), 8.48 (d, J = 2.0 Hz, 2H), 8.06 (s, 2H), 7.69 (dd, J = 8.7, 1.9 Hz, 2H), 4.17 (s, 6H), 1.51 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 128.9, 127.1, 124.9, 124.5, 123.2, 118.6, 105.0, 56.2, 35.2, 31.7; IR (ATR): ν = 2956, 2904, 2866, 1612, 1516, 1458, 1411, 1359, 1250, 1204, 1164, 1116, 1033, 868, 838, 813, 769, 720, 642, 614; MS (EI$^+$): m/z = 400 (100, [M]$^+$), 385 (67), 355 (3), 329 (3), 314 (5), 283 (3), 239 (4), 185 (5), 157 (8), 126 (2); HR-MS (EI$^+$): m/z = 400.2400, calculated for $C_{28}H_{32}O_2$ ([M]$^+$): 400.2402.

7,10-Di-*tert*-butyl-2,3-dimethoxytriphenylene (7i): Flash chromatography (eluent: diethyl ether); yellow solid; yield: 169 mg (0.42 mmol, 85%, 2.20 F, 77% ce); mp 165–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 2.0 Hz, 2H), 8.45 (d, J = 8.7 Hz, 2H), 7.99 (s, 2H), 7.72 (dd, J = 8.6, 2.0 Hz, 2H), 4.13 (s, 6H), 1.61–1.49 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 148.9, 129.1, 127.5, 125.0, 124.1, 122.8, 119.1, 104.7, 56.1, 35.1, 31.6; IR (ATR): ν = 3100, 3002, 2954, 2903, 2866, 1613, 1538, 1501, 1458, 1363, 1307, 1264, 1228, 1201, 1021, 912, 878, 843, 813, 813, 738, 658, 599, 550; MS (EI$^+$): m/z = 400 (100, [M]$^+$), 385 (74), 355 (3), 314 (5), 283 (3), 239 (3), 200 (2), 157 (12), 126 (2, 57 (17); HR-MS (EI$^+$): m/z = 400.2415, calculated for $C_{28}H_{32}O_2$ ([M]$^+$): 400.2402.

7,10-Dichloro-2,3-dimethoxytriphenylene (7j): Flash chromatography (eluent: *n*-pentane/diethyl ether 5:1→3:1→1:1); brown solid; yield: 146 mg (0.41 mmol, 82%, 2.52 F, 65% ce); mp 180–182 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, J = 2.2 Hz, 2H), 8.10 (d, J = 8.9 Hz, 2H), 7.59 (s, 2H), 7.45 (dd, J = 8.8, 2.1 Hz, 2H), 4.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 132.4, 129.2, 128.1, 127.7, 124.2, 123.3, 123.0, 104.2, 56.1; IR (ATR): ν = 3578, 3004, 2930, 2840, 1725, 1609, 1497, 1457, 1414, 1297, 1266, 1203, 1166, 1142, 1098, 1024, 865, 838, 798, 734, 548, 485; MS (EI$^+$): m/z = 356 (100, [M]$^+$), 313 (14), 278 (43), 251 (3), 200 (19), 149 (8), 99 (5); HR-MS (EI$^+$): m/z = 356.0379, calculated for $C_{20}H_{14}Cl_2O_2$ ([M]$^+$): 356.0371.

2,11-Dimethoxy-6-(4-methoxyphenyl)triphenylene (9a):[24a] Flash chromatography (eluent: *n*-pentane/dichloromethane 1:1); white solid; yield: 153 mg (0.39 mmol, 79%, 2.07 F, 77% ce); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (t, J = 2.4 Hz, 1H), 8.52–8.39 (m, 1H), 8.36 (dt, J = 6.3, 3.8 Hz, 2H), 7.98–7.76 (m, 2H), 7.63 (dq, J = 8.8, 2.1 Hz, 3H), 7.22–7.07 (m, 2H), 7.03–6.93 (m, 2H), 3.92 (s, 6H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 158.9, 158.8, 138.5, 138.4, 133.9, 131.2, 130.9, 129.1, 128.8, 127.6, 126.3, 125.0, 124.9, 124.3, 124.2, 123.3, 120.6, 115.7, 115.6, 115.5, 114.9, 114.5, 114.5, 55.6, 55.54, 55.49.

6,11-Dimethoxy-2-(3-methoxyphenyl)triphenylene (9b): Flash chromatography (eluent: *n*-pentane/diethyl ether 5:1→3:1); pale brown solid; yield: 140 mg (0.36 mmol, 72%, 2.06 F, 70% ce); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71 (d, J = 1.9 Hz, 1H), 8.59 (d, J = 8.5 Hz, 1H), 8.44 (dd, J = 9.1, 2.9 Hz, 2H), 8.07 (d, J = 2.6 Hz, 1H), 8.01 (d, J = 2.6 Hz, 1H), 7.85 (dd, J = 8.5, 1.9 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.41–7.30 (m, 2H), 7.28–7.23 (m, 2H), 7.03–6.94 (m, 1H), 4.12–3.97 (m, 6H), 3.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 158.34, 158.31, 142.8, 139.7, 130.2 (2C), 129.9 (2C), 129.2, 126.3, 124.42, 124.37, 124.3, 124.0, 123.9, 121.9, 120.0, 115.9, 115.8, 113.5, 112.7, 106.1, 105.8, 55.6, 55.5, 55.4; IR (ATR): ν = 2956, 2841, 1623, 1561, 1449, 1432, 1396, 1295, 1221, 1159, 1147, 1007, 833, 618; MS (EI$^+$): m/z = 394 (100, [M]$^+$), 363 (9), 331 (7), 276 (5), 198 (6), 142 (3), 91 (5); HR-MS (EI$^+$): m/z = 394.1564, calculated for $C_{27}H_{22}O_3$ ([M]$^+$): 394.1569.

10-(3,4-Dimethoxyphenyl)-2,3,6,7-tetramethoxytriphenylene (9c):[24a] Flash chromatography (eluent: *n*-pentane/ethyl acetate 3:2→1:1); white solid; yield: 217 mg (0.45 mmol, 90%, 2.11 F, 86% ce); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, J = 1.8 Hz, 1H), 8.45 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 10.1 Hz, 2H), 7.74 (dd, J = 8.5, 1.8 Hz, 1H), 7.69 (s, 2H), 7.42–7.27 (m, 2H), 7.04 (d, J = 8.2 Hz, 1H), 4.09 (d, J = 2.7 Hz, 12H), 4.02 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.61, 149.55, 149.5, 149.1 (2C), 149.0, 138.8, 134.8, 129.1, 127.8, 125.2, 124.3, 123.9, 123.6, 123.5, 123.4, 121.0, 120.0, 112.0, 111.2, 104.9, 104.7, 104.4 (2C), 56.3, 56.24, 56.20 (2C), 56.17, 56.1.

6-(3,5-Dimethoxyphenyl)-1,3,10,12-tetramethoxytriphenylene (9d): Flash chromatography (eluent: *n*-pentane/ethyl acetate 5:1); yellow solid; yield: 121 mg (0.25 mmol, 50%, 4.71 F, 21% ce); mp 180–182 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, J = 1.9 Hz, 1H), 8.48 (d, J = 8.5 Hz, 1H), 7.78 (dd, J = 8.4, 1.8 Hz, 1H), 7.59 (dd, J = 13.7, 2.3 Hz, 2H), 6.90 (d, J = 2.3 Hz, 2H), 6.73 (t, J = 2.6 Hz, 2H), 6.54 (t, J = 2.3 Hz, 1H), 4.02 (d, J = 1.9 Hz, 6H), 3.99 (s, 6H), 3.91 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4 (2C), 159.1 (2C), 158.9, 158.8, 143.7, 140.1, 132.3, 132.1, 130.9, 130.0, 128.0, 126.5, 124.1, 122.2, 113.6, 113.3, 106.1, 99.5, 98.7, 98.7, 97.5, 97.3, 56.0 (2C), 55.8, 55.6, 55.5 (2C); IR (ATR): ν = 2927, 2839, 1595, 1540, 1457, 1417, 1388, 1272, 1198, 1151, 4447, 1027, 933, 818; MS (EI$^+$): m/z = 484 (100, [M]$^+$), 441 (15), 397 (22), 364 (26), 293 (7), 249 (5), 242 (12), 213 (10),

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149 (31), 119 (6), 91 (4), 85 (10); HR-MS (EI^+): m/z = 484.1886, calculated for $C_{30}H_{26}O_6$ ($[M]^+$): 484.1886.

2,8,14-Trimethoxyhexabenzo[*bc,ef,hi,kl,no,qr*]coronene (13a): Recrystallisation from ethanol (43 mL); orange solid; yield: 37 mg (60.3 μmol, 63%, 14.3 F, 53% ce); mp >270 °C; IR (ATR): ν = 3051, 2960, 2834, 1606, 1491, 1454, 1412, 1362, 1258, 1209, 1168, 1086, 1017, 795, 758; CHN analysis ($C_{45}H_{24}O_3$, MW: 612.68 g mol^{-1}): found (calculated) C 88.19% (88.22%), H 3.99% (3.95%); HR-MS (FD): m/z = 612.2044, calculated for $C_{45}H_{24}O_3$ ($[M]^+$): 612.1725.

2,8,14-Trimethoxy-5,11,17-trimethylhexabenzo[*bc,ef,hi,kl,no,qr*]coronene (13b): Recrystallisation from ethanol (57 mL); orange solid; yield: 30 mg (45.9 μmol, 51%, 16.2 F, 38% ce); mp >270 °C; CHN analysis ($C_{45}H_{24}O_3$, MW: 612.68 g mol^{-1}): found (calculated) C 87.85% (88.05%), H 4.41% (4.62%); IR (ATR): ν = 2924, 2850, 1712, 1603, 1493, 1456, 1227, 1175, 1071, 1033, 858, 807; HR-MS (FD): m/z = 654.1399, calculated for $C_{48}H_{31}O_3$ ($[M]^+$): 654.2195.

2,8,14-Tri-*tert*-butylhexabenzo[*bc,ef,hi,kl,no,qr*]coronene (13c): Purification was performed by dissolving the crude product in dichloromethane (15 mL) followed by precipitation with methanol (100 mL); yellow solid; yield: 54 mg (78.7 μmol, 69%, 13.9 F, 60% ce); mp >270 °C; CHN analysis ($C_{45}H_{24}O_3$, MW: 612.68 g mol^{-1}): found (calculated) C 93.99% (93.87%), H 6.35% (6.13%); IR (ATR): ν = 2955, 2863, 1604, 1467, 1361, 1254, 1205, 1094, 1019, 942, 903, 869, 800, 729, 664, 605; HR-MS (FD): m/z = 690.3295, calculated for $C_{54}H_{43}$ ($[M]^+$): 690.3295.

Hexabenzo[*bc,ef,hi,kl,no,qr*]coronene (16a):[29] Recrystallisation from chloroform/ethanol (1:1, 100 mL); yellow solid; yield: 254 mg (485 mmol, 95%, 20.1 F, 57% ce); mp >270 °C. IR (ATR): ν = 3013, 1893, 1688, 1607, 1304, 1128, 1128, 952, 840, 762, 538; HR-MS (FD): m/z = 522.1413, calculated for $C_{42}H_{18}$ ($[M+H]^+$): 522.1409.

2,5,8,11,14,17-Hexa-*tert*-butylhexabenzo[*bc,ef,hi,kl,no,qr*]coronene (16b):[3d] Purification was performed by dissolving the crude product in dichloromethane (10 mL) followed by precipitation with methanol (100 mL); orange solid; yield: 425 mg (495 mmol, 99%, 12.9 F, 92% ce); ^{1}H NMR (300 MHz, $CHCl_3$): δ = 9.33 (s, 12 H), 1.85 (s, 54 H); ^{13}C NMR (75 MHz, $CHCl_3$): δ = 149.2, 130.7, 124.2, 120.6, 119.0, 35.9, 32.2.

References

[1] a) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267–1300; b) C. D. Simpson, J. Wu, M. D. Watson, K. Müllen, *J. Mater. Chem.* **2004**, *14*, 494–504; c) S. R. Waldvogel, S. Trosien, *Chem. Commun.* **2012**, *48*, 9109–9119; d) M. Grzybowski, K. Skonieczny, H. Butenschön, D. T. Gryko, *Angew. Chem.* **2013**, *125*, 10084–10115; *Angew. Chem. Int. Ed.* **2013**, *52*, 9900–9930; e) A. Narita, X.-Y. Wang, X. Feng, K. Müllen, *Chem. Soc. Rev.* **2015**, *44*, 6616–6643; f) B. A. G. Hammer, K. Müllen, *Chem. Rev.* **2016**, *116*, 2103–2140.

[2] a) W. J. Scott, J. K. Stille, *J. Am. Chem. Soc.* **1986**, *108*, 3033–3040; b) J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524; c) K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, K. Suzuki, *Tetrahedron* **1982**, *38*, 3347–3354; d) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; e) A. de Meijere, S. Bräse, M. Oestreich, in: *Metal-Catalysed Cross-Coupling Reactions and More*, 1st edn., Vol. 1, Wiley-VCH, Weinheim, **2014**; f) W. Carruthers, I. Coldham, in: *Modern Methods of Organic Synthesis*, 4th edn., Cambridge University Press, Cambridge, **2004**, pp 89–100.

[3] a) P. Rempala, J. Kroulik, B. T. King, *J. Am. Chem. Soc.* **2004**, *126*, 15002–15003; b) P. Rempala, J. Kroulik, B. T. King, *J. Org. Chem.* **2006**, *71*, 5067–5081; c) B. T. King, J. Kroulik, C. R. Robertson, P. Rempala, C. L. Hilton, J. D. Korinek, L. M. Gortari, *J. Org. Chem.* **2007**, *72*, 2279–2288; d) L. Zhai, R. Shukla, S. H. Wadumethrige, R. Rathore, *J. Org. Chem.* **2010**, *75*, 4748–4760.

[4] a) G. Lessene, K. S. Feldman, in: *Modern Arene Chemistry*, 1st edn., (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**, pp 479–534; b) S. R. Waldvogel, D. Mirk, in: *Handbook of C–H Transformations*, Vol. 1. (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, pp 251–276.

[5] a) G. Sartori, R. Maggi, F. Bigi, M. Grandi, *J. Org. Chem.* **1993**, *58*, 7271–7273; b) K. Ding, Q. Xu, Y. Wang, J. Liu, Z. Yu, B. Du, Y. Wu, H. Koshima, T. Matsuura, *Chem. Commun.* **1997**, 693–694.

[6] a) J. Löwe, *Z. Chemie* **1868**, *4*, 603–604; b) R. Scholl, J. Mansfeld, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734–1746; c) R. Scholl, C. Seer, *Liebigs Ann.* **1912**, *394*, 111–117.

[7] a) A. Ronlán, V. D. Parker, *Chem. Commun.* **1970**, 1567–1568; b) L. J. Kricka, A. Ledwith, *Acc. Chem. Res.* **1972**, *5*, 294–297; c) K. Nyberg, *Acta Chem. Scand.* **1973**, *27*, 503–509; d) A. Ronlán, O. Hammerich, V. D. Parker, *J. Am. Chem. Soc.* **1973**, *95*, 7132–7138; e) A. Ronlán, V. D. Parker, *J. Org. Chem.* **1974**, *39*, 1014–1016; f) H. J. Schäfer, in: *Organic Electrochemistry*, 5th edn., (Eds.: O. Hammerich, B. Speiser), CRC Press, Boca Raton, **2016**, pp 705–773.

[8] a) A. Kirste, M. Nieger, I. M. Malkowsky, F. Strecker, A. Fischer, S. R. Waldvogel, *Chem. Eur. J.* **2009**, *15*, 2273–2277; b) A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. G. Waldvogel, *Angew. Chem.* **2010**, *122*, 983–987; *Angew. Chem. Int. Ed.* **2010**, *49*, 971–975; c) A. Kirste, G. Schnakenburg, S. R. Waldvogel, *Org. Lett.* **2011**, *13*, 3126–3129; d) A. Kirste, B. Elsler, G. Schnakenburg, S. R. Waldvogel, *J. Am. Chem. Soc.* **2012**, *134*, 3571–3576; e) B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem.* **2014**, *126*, 5311–5314; *Angew. Chem. Int. Ed.* **2014**, *53*, 5210–5213; f) B. Elsler, A. Wiebe, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Chem. Eur. J.* **2015**, *21*, 12321–12325; g) S. Lips, A. Wiebe, B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem.* **2016**, *128*, 11031–11035; *Angew. Chem. Int. Ed.* **2016**, *55*, 10872–10876; h) A. Wiebe, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem.* **2016**, *128*, 11979–11983; *Angew. Chem. Int. Ed.* **2016**, *55*, 11801–11805.

[9] T. Morofuji, A. Shimizu, J.-i. Yoshida, *Angew. Chem.* **2012**, *124*, 7371–7374; *Angew. Chem. Int. Ed.* **2012**, *51*, 7259–7262.

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[10] a) C. Kübel, K. Eckhardt, V. Enkelmann, G. Wegner, K. Müllen, *J. Mater. Chem.* **2000**, *10*, 879–886; b) C. D. Simpson, G. Mattersteig, K. Martin, L. Gherghel, R. E. Bauer, H. J. Räder, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 3139–3147; c) A. McKillop, A. G. Turrell, D. W. Young, E. C. Taylor, *J. Am. Chem. Soc.* **1980**, *102*, 6504–6512; d) J. B. Aylward, *J. Chem. Soc. B* **1967**, 1268–1270; e) G. A. Olah, G. Liang, *J. Org. Chem.* **1976**, *41*, 2661–2662; f) S. M. Kupchan, A. J. Liepa, V. Kameswaran, R. F. Bryan, *J. Am. Chem. Soc.* **1973**, *95*, 6861–6863; g) S. Yamaguchi, T. M. Swagger, *J. Am. Chem. Soc.* **2001**, *123*, 12087–12088; h) R. Rathore, A. S. Kumar, S. V. Lindeman, J. K. Kochi, *J. Org. Chem.* **1998**, *63*, 5847–5856; i) A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730–2744; j) M. Schubert, S. R. Waldvogel, *Eur. J. Org. Chem.* **2016**, 1921–1936.

[11] a) Y. Kita, M. Gyoten, M. Ohtsubo, H. Tohma, T. Takada, *Chem. Commun.* **1996**, 1481–1482; b) T. Takada, M. Arisawa, M. Gyoten, R. Hamada, H. Tohma, Y. Kita, *J. Org. Chem.* **1998**, *63*, 7698–7706; c) M. Arisava, S. Utsumi, M. Nakajima, N. G. Ramesh, H. Tohma, Y. Kita, *Chem. Commun.* **1999**, 469–470; d) Y. Kita, M. Egi, T. Takada, H. Tohma, *Synthesis* **1999**, 885–897; e) H. Tohma, H. Morioka, S. Takizawa, M. Arisawa, Y. Kita, *Tetrahedron* **2001**, *57*, 345–352; f) T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma, Y. Kita, *Angew. Chem.* **2005**, *117*, 6349–6352; *Angew. Chem. Int. Ed.* **2005**, *44*, 6193–6196; g) K. Morioku, N. Morimoto, Y. Takeuchi, Y. Nishina, *Nature* **2016**, *6*, 25824–25831; h) T. Broese, R. Francke, *Org. Lett.* **2016**, *18*, 5896–5899.

[12] L. Zhai, R. Shukla, R. Rathore, *Org. Lett.* **2009**, *11*, 3474–3477.

[13] M. S. Newman, V. K. Khanna, *Org. Prep. Proc. Int.* **1985**, *17*, 422–423.

[14] A. E. Wendlandt, S. S. Stahl, *Angew. Chem.* **2015**, *127*, 14848–14868; *Angew. Chem. Int. Ed.* **2015**, *54*, 14638–14658.

[15] R. Francke, T. Quell, A. Wiebe, S. R. Waldvogel, in: *Organic Electrochemistry*, 5th edn., (Eds.: O. Hammerich, B. Speiser), CRC Press, Boca Raton, **2016**, pp 981–1033.

[16] a) G. Hilt, *Chem. Rec.* **2014**, *14*, 386–396; b) J. R. Kuttner, G. Hilt, *Macromolecules* **2014**, *47*, 5532–5541; c) P. Röse, G. Hilt, *Synthesis* **2016**, *48*, 463–492.

[17] a) Q. Fan, C. Wang, Y. Han, J. Zhu, J. Kuttner, G. Hilt, J. M. Gottfried, *ACS Nano* **2014**, *8*, 709–718; b) J. Shang, Y. Wang, M. Chen, J. Dai, X. Zhou, J. Kuttner, G. Hilt, Y. Shao, J. M. Gottfried, K. Wu, *Nat. Chem.* **2015**, *7*, 389–393; c) Q. Fan, J. Dai, T. Wang, J. Kuttner, G. Hilt, J. M. Gottfried, J. Zhu, *ACS Nano* **2016**, *10*, 3747–3754.

[18] M. Danz, R. Tonner, G. Hilt, *Chem. Commun.* **2012**, *48*, 377–379.

[19] P. W. Crawford, E. Carlos, J. C. Ellegood, C. C. Cheng, Q. Dong, D. F. Liu, Y. L. Luo, *Electrochim. Acta* **1996**, *41*, 2399–2403.

[20] K. Tetsuya, K. Jun, K. Kengo, T. Hiroyuki, (Canon Kabushiki Kaisha), U.S. Patent 20130037788, **2012**.

[21] S. R. McLaren, D. J. Tate, O. R. Lozman, G. H. Mehl, R. J. Bushby, *J. Mater. Chem. C.* **2015**, *3*, 5754–5763.

[22] M. Schubert, J. Leppin, K. Wehming, D. Schollmeyer, K. Heinze, S. R. Waldvogel, *Angew. Chem.* **2014**, *126*, 2527–2530; *Angew. Chem. Int. Ed.* **2014**, *53*, 2494–2497.

[23] a) S. R. Waldvogel, D. Mirk, *Tetrahedron Lett.* **2000**, *41*, 479–4772; b) M. C. Schopohl, A. Faust, D. Mirk, R. Fröhlich, O. Kataeva, S. R. Waldvogel, *Eur. J. Org. Chem.* **2005**, 2987–2999; c) M. Schubert, P. Franzmann, A. Wünsche von Leuoldt, K. Koszinowski, K. Heinze, S. R. Waldvogel, *Angew. Chem.* **2016**, *128*, 1168–1172; *Angew. Chem. Int. Ed.* **2016**, *55*, 1156–1159.

[24] a) L. Xu, R. Yu, Y. Wang, J. Chen, Z. Yang, *J. Org. Chem.* **2013**, *78*, 5744–5750; b) M. Rehan, S. Maity, L. Kumar Morya, K. Pal, P. Ghorai, *Angew. Chem.* **2016**, *128*, 7859–7863; *Angew. Chem. Int. Ed.* **2016**, *55*, —7728-7732.

[25] a) G. Hilt, T. Vogler, W. Hess, F. Galbiati, *Chem. Commun.* **2005**, 1474–1475; b) G. Hilt, W. Hess, T. Vogler, C. Hengst, *J. Organomet. Chem.* **2005**, *690*, 5170–5181; c) G. Hilt, C. Hengst, W. Hess, *Eur. J. Org. Chem.* **2008**, 2293–2297.

[26] A. Pradhan, P. Dechambenoit, H. Bock, F. Durola, *Angew. Chem.* **2011**, *123*, 12790–12793; *Angew. Chem. Int. Ed.* **2011**, *50*, 12582–12585.

[27] X. Cong, H. Tang, X. Zeng, *J. Am. Chem. Soc.* **2015**, *137*, 14367–14372.

[28] M. L. Hossain, F. Ye, Z. Liu, Y. Xia, L. Zhou, Y. Zhang, J. Wang, *J. Org. Chem.* **2014**, *79*, 8689–8699.

[29] G. Brancolini, F. Negri, *Carbon* **2004**, *42*, 1001–1005.

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Efficient Oxidative Coupling of Arenes *via* Electrochemical Regeneration of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) under Mild Reaction Conditions

Adv. Synth. Catal. **2017**, *359*, 1 – 15

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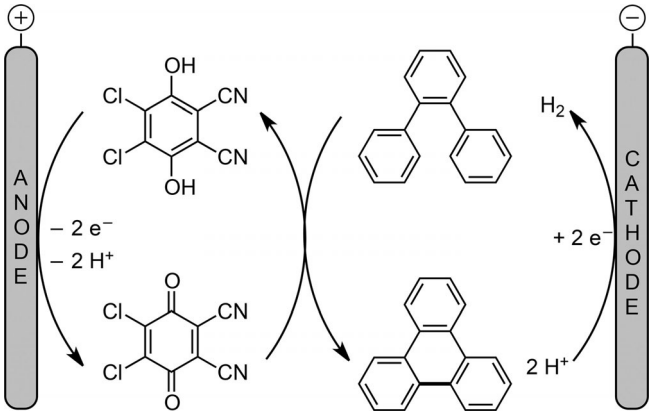

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