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Fused-Ring Systems

A Versatile One-Pot Access to Cyanoarenes from *ortho*- and *para*-Quinones: Paving the Way for Cyanated Functional Materials

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Abstract: A generally applicable direct synthesis of cyanoarenes from quinones is presented. Particular emphasis is placed on the preparation of precursors and target molecules relevant for organic materials, including halogenated cyanoarenes and larger cyanated acenes. The reaction and work-up protocols are adjusted for the challenges presented by the different substrates and products. Screening results of the initial reaction optimization are given to further facilitate adaptation to other synthetic problems. The universality of the reaction is finally highlighted by successful substitution of *para*-quinones by an *ortho*-quinone as the starting material.

Introduction

In the past few decades, polycyclic aromatic hydrocarbons, and in particular acenes, have attracted tremendous attention as organic functional materials both theoretically and experimentally.[1] Among these materials, cyanated compounds take on a particular role as promising candidates for air-stable n-type and ambipolar organic field effect transistors (OFETs). This is due to the low internal reorganization energies for electron and hole transfer, large intermolecular electronic couplings, high electron affinities, and overall small HOMO–LUMO gaps, which are all characteristics predicted by computational studies.[2] These theoretical works on larger cyanated acenes are complemented by only a single experimental investigation of the material properties of 5,12-dicyanonaphthacene and 6,13-dicyanopentacene, confirming the significantly low HOMO and LUMO levels and demonstrating the fabrication of OFET devices with ambipolar properties.[3] The absence of further experimental results can clearly be attributed to a lack of convenient synthetic access to this type of molecules.

Aside from the applicability of the larger cyanated acenes for organic electronics, smaller cyanated acenes also play an important role as photosensitizers in light-mediated reactions.[4] In particular, 9,10-dicyanoanthracene has been examined as a photosensitizer in photooxidations of olefins and in other photochemical reactions such as C–C bond cleavage reactions of lignin β-1 model compounds and in the preparation of the anti-malaria drug Artemisinin.[5] Moreover, cyanoarenes have also been employed as strong electron acceptors in several investigations of bimolecular photoinduced electron transfer reactions,[6] and for two-photon absorption.[7]

As the nitrile represents a versatile functional group in synthetic chemistry, a large number of secondary products can be synthesized from appropriately substituted cyanoarenes. For 1,4-dicyanobenzenes and 9,10-dicyanoanthracenes, the known modifications include the preparation of the corresponding aldehydes,[8] thioamides,[9] various heterocyclic compounds,[10] and nucleophilic benzylation by using readily available zinc reagents.[11] Moreover, dicyanoarenes have been applied as ligands in π-stacked metalloparacyclophanes.[12]

Despite these manifold applications of cyanoarenes, preparative approaches, until recently, have often involved either several synthetic steps or labor-intensive purification procedures.[3,10a,13] This was overcome when we reported a synthetic method for the conversion of quinones to cyanoarenes via silylated cyanohydrin intermediates in a one-pot reaction.[14] A benefit of using quinones as the starting materials is their (commercial) availability in a wide range of different substitution patterns, including halogenated derivatives. In principle, this novel synthesis allows the preparation of cyanoarenes with substitution patterns not accessible so far or accessible only by multi-step procedures.

However, the reported method has some disadvantages. Yields are moderate, the catalyst for the first reaction step—cesium fluoride—is highly hygroscopic and a large excess of trimethylsilyl cyanide (TMSCN) is required as a reagent. Moreover, this excess of TMSCN has to be carefully controlled by in situ IR spectroscopic measurements to enable a successful one-pot conversion of 1,4-benzoquinone, which is prone to side reactions such as conjugate addition and rearrangement. Thus, optimization of the reaction conditions is required prior to investigations of the substrate scope.

As cyanoarenes are particularly useful for organic materials chemistry, the subsequent focus on the synthesis of precursors and substrates for this field of research is considered beneficial.

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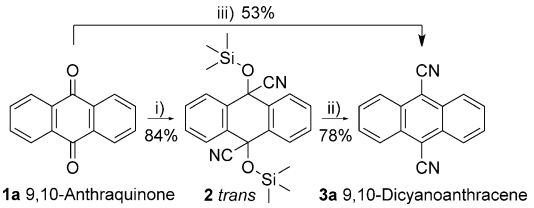
Promising molecules include halogenated cyanoarenes for transition-metal-catalyzed cross-coupling reactions, which are frequently used in the synthesis of functional organic materials,[15] and silylated alkynyl-functionalized aromatic compounds as they belong to an intensely studied substance class.[1b,c] Moreover, after desilylation, the alkynyl substituents allow for a modification by Sonogashira cross-coupling reactions or copper(I)-catalyzed azide–alkyne cycloadditions,[16] which makes alkynyl-functionalized cyanoarenes interesting precursors for further reactions. The applicability of the reaction conditions to larger substrates can be tested and optimized with the example of 6,13-pentacenequinone, and the universality can be tested by replacing *para*-quinone with *ortho*-quinone as the starting material.

Results and Discussion

Reaction optimization

Both reaction steps from quinones to cyanoarenes (Scheme 1, i and ii) were screened individually to improve the reaction conditions and to develop a convenient and generally applicable procedure. However, applicability as a one-pot procedure was kept in mind. 9,10-Anthraquinone **1a** was used for the solvent and catalyst screening of the first reaction step (Scheme 1, i) as conversion of this substrate was found to be more ambitious than conversion of 1,4-benzoquinone **1b**. The results of this screening are given in Table 1.



Scheme 1. Individually screened reaction steps from quinones to cyanoarenes by using 9,10-anthraquinone **1a** as the starting material: cyanohydrin formation (i) (Table 1), reductive aromatization (ii) (Table 2); synthesis finally carried out as a one-pot reaction (iii) (Table 3).

Initially, the temperature dependence of the reaction time was investigated at otherwise identical conditions as in our previous report (Table 1, top). It was found that the reaction proceeds considerably faster at room temperature (rt) than at 0 °C and −15 °C; nevertheless, at all temperatures full conversion of both carbonyl groups of starting material **1a** was observed by GCMS measurements. The experiments at lower temperatures revealed that both the *trans* and the *cis* isomer of **2** are formed, but the latter is converted to the *trans* isomer as the reaction proceeds (stereochemistry confirmed by X-ray diffraction, Figure 1). The rate of this isomerization strongly depends on the reaction temperature. At −15 °C, the isomerization remained incomplete even after a reaction time of 18 h.

When adding less trimethylsilyl cyanide (TMSCN, 2.6 equiv), the reaction remained incomplete at room temperature. At 0 °C, full conversion was observed. A lower catalyst loading of

Table 1. Catalyst, solvent, and temperature screening of the reaction from 9,10-anthraquinone **1a** to cyanohydrin intermediate **2** (Scheme 1, i).[a]

Catalyst (equiv)	TMSCN [equiv]	Solvent (M)[b]	*T*	Reaction time[c]
CsF (0.2)	3.0	MeCN (0.5)	rt	2 h
CsF (0.2)	3.0	MeCN (0.5)	0 °C	5 h
CsF (0.2)	3.0	MeCN (0.5)	−15 °C	18 h[d]
CsF (0.2)	2.6	MeCN (0.5)	rt	incomp. conversion
CsF (0.2)	2.6	MeCN (0.5)	0 °C	6 h
CsF (0.1)	3.0	MeCN (0.5)	rt	5 h
CsF (0.1)	3.0	THF (0.5)	rt	30 h
Cs_2CO_3 (0.1)	3.0	MeCN (0.5)	0 °C	6 h
KF (0.1)	3.0	MeCN (0.5)	0 °C	no conversion
K_2CO_3 (0.1	3.0	MeCN (0.5)	0 °C	27 h[d]
no catalyst	3.0	MeCN (0.5)	0 °C	no conversion
Cs_2CO_3 (0.1)	3.0	CH_2Cl_2 (0.5)	0 °C	no conversion
Cs_2CO_3 (0.01)	2.1	MeCN (0.5)	0 °C	40 h
K_2CO_3 (0.05)	3.0	DMF (0.3)	0 °C	1 h
K_2CO_3 (0.02)	2.2	DMF (2.0)	0 °C	3 h
K_2CO_3 (0.05)	3.0	DMSO (0.3)	rt	20 min
K_2CO_3 (0.05)	2.6	DMSO (0.3)	rt	20 min
Cs_2CO_3 (0.05)	3.0	DMF (0.3)	0 °C	1 h
Cs_2CO_3 (0.05)	3.0	DMSO (0.3)	rt	3 h
no catalyst	3.0	DMSO (0.3)	rt	no conversion
KCN (0.05)	2.05	DMF (2.0)	0 °C	4 h
KCN (0.05)	**2.05**	**DMF (2.0)**	**rt**	**3 h**
no catalyst	2.05	DMF (2.0)	rt	no conversion

[a] Reactions carried out on a scale of 0.5 mmol to 1.0 mmol. [b] Concentration of starting material **1a** given in brackets. [c] Reaction time until full conversion of both carbonyl groups of starting material **1a**, determined by GCMS measurements. [d] Incomplete conversion of *cis* isomer into *trans* isomer.

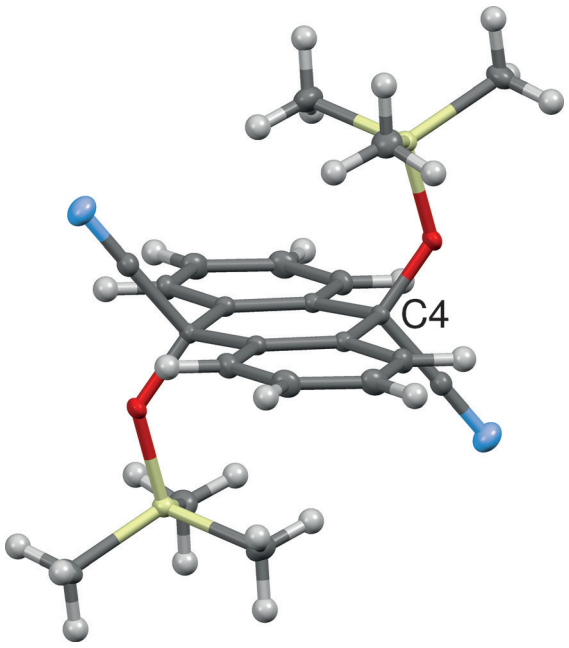


Figure 1. Molecular structure of the cyanohydrin intermediate **2**. C (gray), N (blue), O (red) and Si (yellow) atoms are represented by ellipsoids drawn at the 50% probability levels, H atoms by white spheres of arbitrary radius.

0.1 equivalents instead of 0.2 equivalents required longer reaction times but still showed full conversion at room temperature. The same experiment was successfully carried out in tetrahydrofuran (THF) with a considerably longer reaction time of 30 h.

In a subsequent catalyst screening, Cs_2CO_3 was found to perform almost equally as well as CsF. This finding is particularly useful because of the difficult handling of CsF owing to its strong hygroscopic behavior. Furthermore, K_2CO_3 also enabled full conversion within 27 h.

We attributed the long reaction time with K_2CO_3 to its low solubility in acetonitrile (MeCN) and therefore tested dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) as solvents. In addition, we reduced the catalyst loading to 0.05 equivalents or less. These reactions (except for the blank test) showed full conversion in no longer than 3 h at 0 °C (DMF) and 20 min at room temperature (DMSO, m.p. 19 °C).

All of the above-mentioned catalysts are also known to act as deprotection agents in desilylation reactions. To reduce the required excess of TMSCN at room temperature, we tested KCN as the catalyst. The application of this reagent is expected to result in back-formation of TMSCN if desilylation occurs. Indeed, by using only 0.05 equivalents KCN, we were able to achieve full conversion to the cyanohydrin intermediate **2** even at room temperature and with as little as 0.05 equivalents excess of TMSCN. DMF was used as the solvent because of its expected suitability for one-pot reactions: some DMF was found necessary for a successful aromatization in the one-pot reactions in our previous work. However, to enable an efficient aromatization, the amount of DMF has to be kept low.

By using these final conditions, the *trans* intermediate **2** was isolated in yields of 84%. X-ray diffraction of single crystals grown from fluorobenzene confirmed the expected stereochemistry. Compound **2** crystallizes in space group $P\bar{1}$. One crystallographically unique molecule (Figure 1) is located on a center of inversion, reflecting the *trans* configuration of the molecule. The annulated ring system deviates distinctly from planarity [distance of the central C4 atom to the least squares (LS) plane defined by the atoms of the benzene ring: 0.0821(11) Å], in contrast to the cyclohexadiene analog,[17] which is virtually flat. The tetrahedral angles around C4 are distorted owing to ring strain [O-C-CN: 104.51(9)°, cyclohexadiene analog: 104.95(8)°]. Neither inter-molecular non-classical hydrogen-bonding, nor π–π stacking was observed, owing to the bulky TMS groups.

In the first report on the synthesis of cyanoarenes by reductive aromatization, we described the possibility of avoiding the formation of reaction byproducts by using PCl_3 instead of $POCl_3$ as the aromatization reagent for the second reaction step (Scheme 1, ii).[14] However, increasing amounts of DMF in the solvent mixture spoil this effect. This is particularly obstructive as the addition of DMF was found to be necessary for the aromatization step in one-pot reactions. Furthermore, the resulting byproducts when converting 1,4-benzoquinone **1b** into 1,4-dicyanobenzene **3b** could not be separated by column chromatography. We therefore tested the weaker Lewis acid PBr_3 for aromatization of intermediate **2** and indeed obtained promising results, especially in MeCN (Table 2). By using PBr_3 instead of PCl_3 the yield of **3a** was increased to 71% at room temperature and 78% at 0 °C. Carrying out the reaction in dichloromethane (CH_2Cl_2) resulted in a yield of 55%. The reaction in THF did not afford any product, although PBr_3 has been used as an aromatization reagent in THF before.[18] Aromatization in DMF and DMSO was also not successful.

Table 2. Reagent, solvent, and temperature screening of the aromatization step from **2** to **3a** (Scheme 1, ii) by addition of 0.5 mmol reagent (PCl_3 or PBr_3) and 0.25 mmol DMF to 0.5 mmol of **2** in 1 mL solvent.

Reagent	Solvent	*T*	Reaction time [h][a]	Isolated yield [%][b]
PCl_3	MeCN	rt	5	55
PBr_3	MeCN	rt	2	71
PBr_3	MeCN	0 °C	8	78
PBr_3	CH_2Cl_2	0 °C	31	55
PBr_3	THF	0 °C	≫120	–
PBr_3	DMF	rt	≫120	–
PBr_3	DMSO	rt	≫120	–

[a] Reaction time until full conversion of **2**, determined by GCMS measurements. [b] Isolation of **3a** by dilution of the reaction mixture with CH_2Cl_2 and subsequent filtration over a thick pad of silica with CH_2Cl_2 as the eluent.

Further investigations focused on the one-pot conversion of the quinones to cyanoarenes (Scheme 1, iii), because insufficient stability of (silylated) cyanohydrins has been observed during work-up. The first reaction step was carried out by using KCN as the catalyst and as little DMF as possible. The reaction was diluted with MeCN for the second reaction step and PBr_3 was added. Without the dilution with MeCN no product formation was achieved. When using DMSO for the first reaction step, no cyanoarene formation was observed in the second step.

In contrast to the screening reactions in pure solvents, the one-pot reactions had to be heated to 50 °C after the first reaction step for efficient aromatization. Work-up was again achieved by diluting the reaction with CH_2Cl_2 and filtering over a thick pad of silica with CH_2Cl_2 as the eluent.

The new conditions not only enabled significantly higher yields for the conversion of both 9,10-anthraquinone **1a** and 1,4-benzoquinone **1b** to 9,10-dicyanoanthracene **3a** and 1,4-dicyanobenzene **3b** than previously reported (**3a**: 27%, **3b**: 30%), but also helped to reduce the reaction times and to avoid the formation of inseparable byproducts in the reaction towards **3b** (Table 3).

Synthesis of halogenated and borylated cyanoarenes and their applications in Suzuki coupling reactions

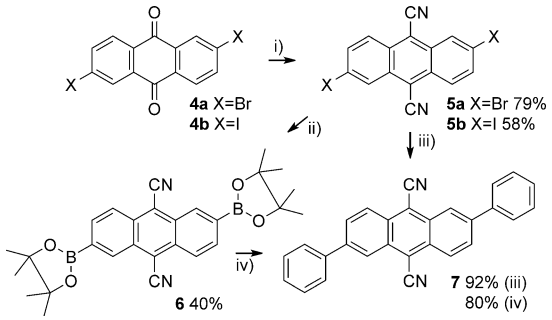
Despite the promising properties of 9,10-dicyanoanthracenes, aryl-substituted derivatives have only been reported in two patents, which claim the (multi-step) synthesis of such compounds.[19] This is attributed to the lack of easily accessible halogenated dicyanoanthracene precursors for cross-coupling reactions. So far, 2-chloro-9,10-dicyanoanthracene is the only known halogenated dicyanoanthracene.[19a]

Table 3. One-pot conversion of 9,10-anthraquinone **1a** and 1,4-benzoquinone **1b** to 9,10-dicyanoanthracene **3a** (Scheme 1, iii) and 1,4-dicyanobenzene **3b**.[a]

Starting material	Product	Reagent	Reaction time[b]	Isolated yield [%]
1a	**3a**	PCl_3	3 h + 2 h	44
1a	**3a**	PBr_3	3 h + 3 h	53
1b	**3b**	PCl_3	10 min + 30 min	no pure product[c]
1b	**3b**	PBr_3	10 min + 30 min	40

[a] Carried out on a 0.50 mmol scale by using 2.05 equiv TMSCN, 0.05 equiv KCN, and 0.25 mL DMF for the first reaction step (at rt) and adding 1.50 mL MeCN and 1.20 equiv reagent (PCl_3 or PBr_3) for the second reaction step (at 50 °C). [b] Reaction time of first and second step. [c] Inseparable byproduct.

Following the optimized one-pot protocol enabled the synthesis of novel brominated and iodinated 9,10-dicyanoanthracenes **5a** and **5b** from the respective anthraquinones (Scheme 2, i). The work-up procedure, however, had to be modified to achieve good yields for these weakly soluble compounds: purification was carried out by repeated washing of the solids with MeCN in the reaction flask. The crude products were then collected by filtration and purified by trituration in boiling toluene. Omitting the washing of the solids results in impurities, which we assume originate from polymerization of phosphoric side products and which cannot be removed by trituration in toluene.

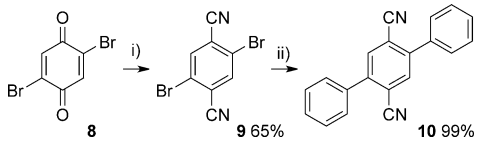


Scheme 2. i) Synthesis of 2,6-dibromo- and 2,6-diiodo-9,10-dicyanoarenes **5a** and **5b**; conditions: TMSCN, KCN, DMF, 3 h, rt; PBr_3, MeCN, 3 h, 50 °C; 153/140 mg. ii) Preparation of dicyanoanthraceneboronic ester **6** by cross-coupling of **5a** with bis(pinacolato)diboron; conditions: $[Pd(PPh_3)_4]$, potassium acetate, DMSO, argon, 6 h, 85 °C, 48 mg. iii and iv) Suzuki coupling of **5a** with phenylboronic acid (conditions: $[Pd(PPh_3)_4]$, aq. K_2CO_3, THF, argon, 3 h, reflux, 87 mg) and **6** with bromobenzene (conditions: $[Pd(PPh_3)_4]$, aq. K_2CO_3, THF, argon, 3 h, 65 °C, 15 mg).

Applying common Suzuki conditions for the coupling of **5a** with phenylboronic acid, we were able to demonstrate the synthesis of 2,6-diphenyl-9,10-dicyanoanthracene **7** in excellent yields (Scheme 2, iii). The same compound was obtained by coupling of dicyanoanthraceneboronic ester **6** with bromobenzene (Scheme 2, iv). This formal exchange of the functional groups is expected to be particularly useful if the boronic acid or ester for a Suzuki coupling with **5a** or **5b** cannot be prepared. Moreover, **6**, which we obtained by coupling **5a** with bis(pinacolato)diboron (Scheme 2, ii), is useful, for example, for the synthesis of substance libraries of aryl-substituted dicyanoanthracenes. That way, the preparation of larger numbers of different boronic acids or esters can be avoided.

The reactions from **4a** to **7** represent a versatile general strategy to aryl-substituted dicyanoanthracenes. Halogenated anthraquinones like **4a** and **4b** can be prepared from amino- and diamino-9,10-anthraquinones,[20] which are commercially available with any possible substitution pattern.

By using 2,5-dibromobenzoquinone **8**, which can be easily obtained on a multigram scale,[21] the novel procedure also allowed for an efficient one-pot synthesis of 1,4-dibromo-2,5-dicyanobenzene **9** (Scheme 3, i). The short total reaction time and the facile work-up by direct filtration over silica enabled preparation from start to finish in less than 3 h. Suzuki coupling with phenylboronic acid was again carried out in excellent yields by applying the same reaction conditions as for the coupling of **5a** (Scheme 3, ii).



Scheme 3. i) Synthesis of 1,4-dibromo-2,5-dicyanobenzene **9** from 2,5-dibromobenzoquinone **8**; conditions: TMSCN, KCN, DMF, 40 min, rt; PBr_3, MeCN, 1 h, 50 °C; 93 mg. ii) Suzuki coupling of **9** with phenylboronic acid; conditions: $[Pd(PPh_3)_4]$, aq. K_2CO_3, THF, argon, 6 h, reflux, 69 mg.

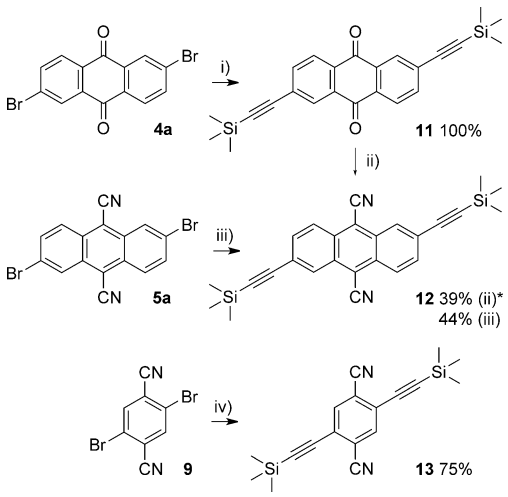
Synthesis of alkynyl-substituted cyanoarenes

Moving from aryl- to alkynyl-substituted 9,10-dicyanoanthracenes, there has not been a single compound reported in the scientific literature so far. In our opinion, this is also owing to the lack of easily accessible halogenated dicyanoanthracene precursors for cross-coupling reactions.

We first tried to synthesize alkynyl-substituted 9,10-dicyanoanthracene **12** from the suitably substituted anthraquinone **11** (Scheme 4, ii), which was obtained from **4a** in excellent yields (Scheme 4, i). Indeed, by following the optimized one-pot protocol, **12** was obtained. However, impurities of starting material **11** could not be removed, neither by column chromatography nor by crystallization.

Fortunately, the Sonogashira coupling approach using **5a** as the substrate also resulted in **12** (Scheme 4, iii) when using a 5:1 mixture of THF and diisopropylamine as solvent.

Yields for the conversion of 1,4-dibromo-2,5-dicyanobenzene **9** to the corresponding alkynyl-substituted dicyanobenzene derivative **13** (Scheme 4, iv) were high when using triethylamine as the solvent. Single crystals of **13** were obtained by solvent evaporation from a solution in chloroform and ethanol and measured. Compound **13** crystallizes in space group $P2_1/c$ with one crystallographically unique molecule (Figure 2a) located in a general position. The C≡C-Si angles deviate significantly from linearity [172.7(2)° and 174.3(2)°]. The molecules are arranged in layers parallel to (100), which connect through the TMS groups (Figure 2b). Besides these van-der-Waals interactions, no additional supramolecular features are observed.



Scheme 4. i) Synthesis of 2,6-bis[(trimethylsilyl)ethynyl]-9,10-anthraquinone **11**; conditions: trimethylsilylacetylene, $[PdCl_2(PPh_3)_2]$, CuI, triethylamine, argon, overnight, 40 °C; 368 mg. ii and iii) Preparation of **12** from **11** (conditions: TMSCN, KCN, DMF, 24 h, rt; PBr_3, MeCN, overnight, 50 °C; 42 mg, *corrected yield) and from **5a** (conditions: trimethylsilylacetylene, $[PdCl_2(PPh_3)_2]$, CuI, 5:1 THF/diisopropylamine, argon, 1 h, reflux; 183 mg). iv) Synthesis of 1,4-dicyano-2,5-bis[(trimethylsilyl)ethynyl]benzene **13**; conditions: trimethylsilylacetylene, $[PdCl_2(PPh_3)_2]$, CuI, triethylamine, argon, 6 h, 50 °C; 120 mg.

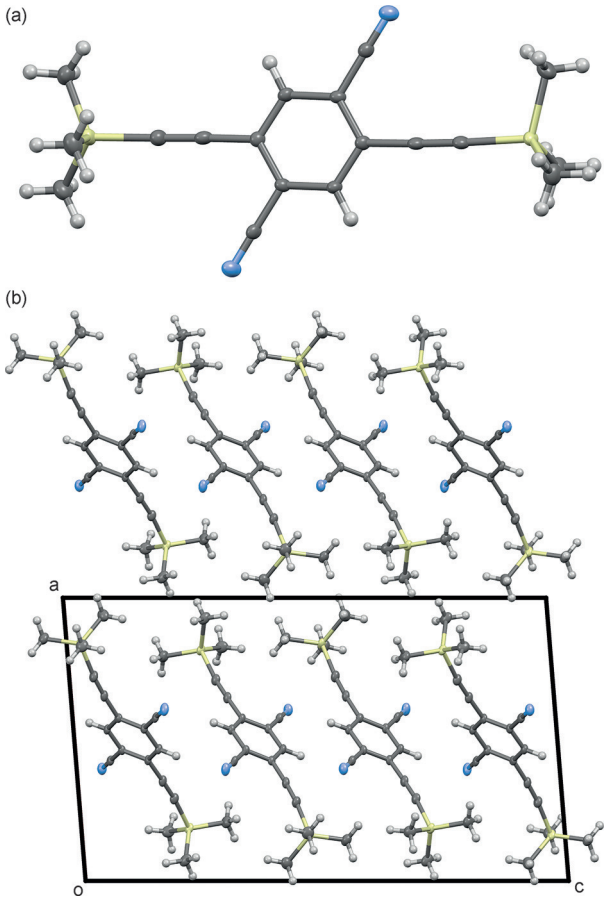


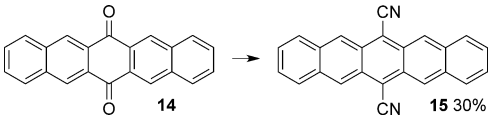
Figure 2. a) Molecular structure and b) packing of 1,4-dicyano-2,5-bis[(trimethylsilyl)ethynyl]benzene **13** viewed down [010]. Atom designations as in Figure 1.

Facilitating the synthesis of 6,13-dicyanopentacene

In 2011, Katsuta et al. reported a five-step synthesis of 6,13-dicyanopentacene **15** starting from pentacene.[3] In their opinion, a preparation of this air-stable ambipolar field-effect transistor material by other research groups has "not been achieved due to […] synthetic difficulties".

We aimed for a simplified preparation of this compound from 6,13-pentacenequinone **14** by following the optimized one-pot protocol (Scheme 5). However, we experienced synthetic difficulties:

Hardly any formation of the cyanohydrin intermediate was observed when using KCN, CsF, Cs_2CO_3, or K_2CO_3 as the catalyst. This was overcome by adding a suspension of LiCN in TMSCN instead. The suspension was prepared by addition of *n*-butyllithium to a slightly increased excess of TMSCN at room temperature and was added to precooled 6,13-pentacenequinone **14** at 0 °C with some DMF. After 6 h at 0 °C complete intermediate formation was observed by TLC analysis.



Scheme 5. Synthesis of 6,13-dicyanopentacene **15**; conditions: TMSCN, *n*BuLi, argon, 15 min, rt; **14**, DMF, argon, 6 h, 0 °C; PBr_3, CH_2Cl_2, argon, overnight, 0 °C; 49 mg.

Yields for the subsequent aromatization were very low at 50 °C owing to back-formation of **14**. However, no aromatization was observed when we maintained the temperature at 0 °C for increased stability of the cyanohydrin intermediate. By adding CH_2Cl_2, which is also a suitable solvent for the aromatization (Table 2), instead of MeCN for increased solubility of the intermediate, significantly better results were obtained. Even at 0 °C full conversion was observed overnight.

Purification was achieved by evaporation of the solvent and volatile side products and subsequent column chromatography. By following this protocol, 6,13-dicyanopentacene **15** was obtained in yields of 30% (Katsuta et al.: 26% overall yield).

The novel procedure enables us to obtain **15** in a single reaction. Furthermore, costs for the starting material **14** are significantly lower than for pentacene, which was used by Katsuta et al. In general, we have demonstrated the great potential of this reaction sequence in the synthesis of large cyanoarenes for applications in organic electronics.

Single crystals of **15** were grown from a solution in a mixture of petroleum ether (PE) and CH_2Cl_2. The long dark needles were subjected to X-ray diffraction. Compound **15** crystallizes in space group $P\bar{1}$. One crystallographically unique molecule (Figure 3a) is located on a center of inversion. As expected, the pentacene core is virtually flat, with a largest deviation from the LS plane of 0.0222(8) Å for the C1 atom. The CN group is slightly inclined with respect to the pentacene core [distance to LS plane: N1: 0.1677(8) Å, C12: 0.0841(8) Å; angle C≡N to LS plane: 4.19(6)°]. The molecules are stacked in

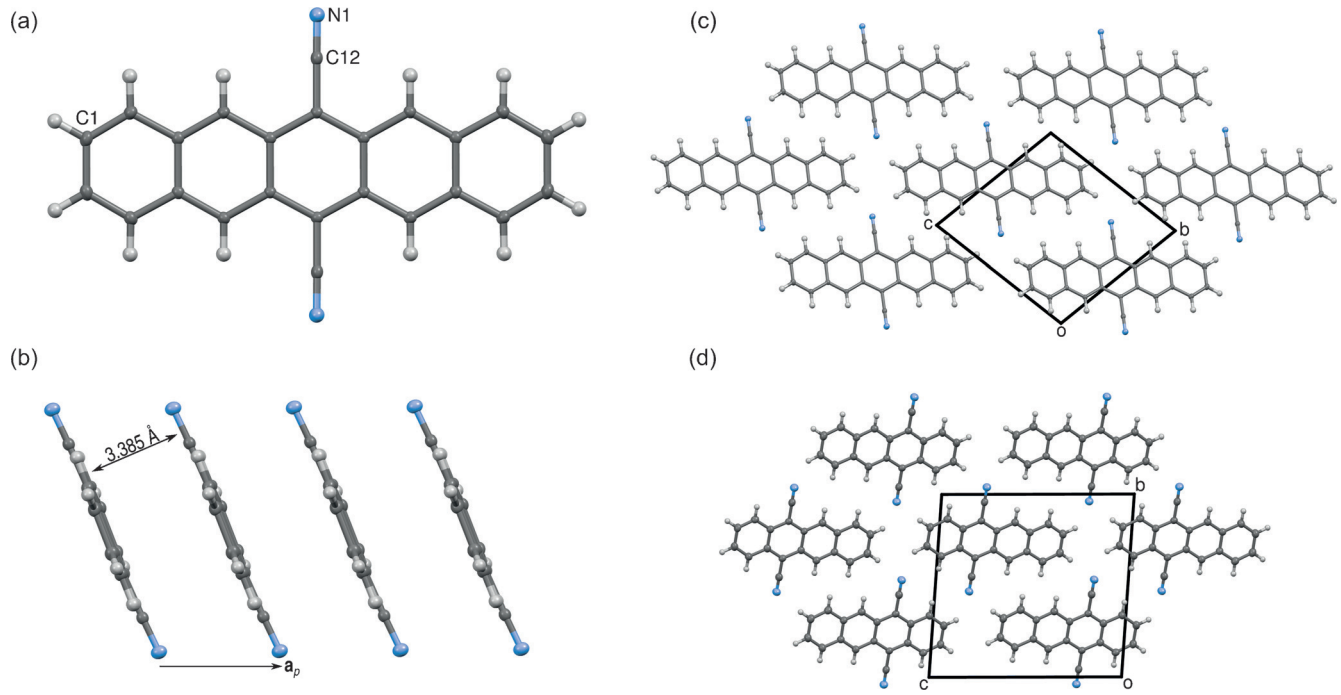


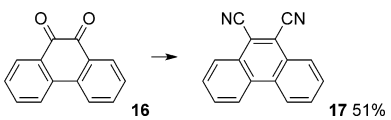
Figure 3. a) Molecular structure, b) rods of π-stacked molecules, and c) packing of 6,13-dicyanopentacene **15** viewed down [100]. d) Packing of 5,12-dicyanonaphthacene viewed down [100] (coordinates taken from Katsuta et al.[3]). Atom designations as in Figure 1.

a face-to-face slipped manner to rods extending along the [100] direction (Figure 3b). The small distance between the LS planes of 3.385 Å indicates significant π–π interactions. Thus, **15** exhibits a packing motif that is desirable for organic electronics applications.[1b] The rods are arranged in a brick wall pattern (Figure 3c), where adjacent rods are offset along the [100] direction and the CN groups protrude into the free space between adjacent rods. 5,12-Dicyanonaphthacene crystallizes in an analogous structure (Figure 3d) with slightly enlarged LS plane distances of 3.392 Å.[3]

Conversion of *ortho*-quinones to cyanoarenes

Considering the effort for the published syntheses of 9,10-dicyanophenanthrene **17**,[11,22] it becomes clear that a direct conversion of *ortho*-quinones to cyanoarenes is a valuable extension of the reaction scope of the presented one-pot protocol.

We were able to carry out such a synthesis of **17** from 9,10-phenanthrenequinone **16** (Scheme 6) by using the same optimized reaction protocol as for the preparation of dicyanoanthracene **3a**. The achieved yields were similar to the synthesis of **3a**. Crystals of **17** were grown from toluene and subjected to X-ray diffraction. Compound **17** crystallizes in space group



Scheme 6. Synthesis of 9,10-dicyanophenanthrene **17**; conditions: TMSCN, KCN, DMF, 1 h, rt; PBr_3, MeCN, overnight, 50 °C; 58 mg.

*C*2/*c*. One crystallographically unique molecule (Figure 4a) is located on a twofold rotation axis. In contrast to **15**, the CN groups are virtually coplanar with the phenanthrene ring system [distance to LS plane: N1: 0.0044(10) Å, C8: 0.0029(9) Å; angle C≡N to LS plane: 0.08(7)°]. The molecules are stacked in a face-to-face slipped manner to rods extending along the [001] direction (Figure 4b). Adjacent molecules are related by inversion and therefore the CN groups face opposite directions. The distance between the LS planes defined by the phenanthrene atoms of the adjacent molecules is 3.414 Å, larger than in the case of **15**. The rods are arranged in a checkerboard pattern, where adjacent rods are offset along the [001] direction (Figure 4c).

Conclusion

By using 9,10-anthraquinone as a model compound, we were able to develop a convenient and reliable one-pot procedure for the synthesis of cyanoarenes from quinones.

Halogenated cyanoarenes can be synthesized, purified, and used for cross-coupling reactions despite the low solubility of some of these compounds after minor adaptation of the procedure.

Preparation of alkynyl-substituted cyanoarenes is possible either by Sonogashira coupling of the halogenated cyanoarenes or directly from the respective quinones. However, purification is difficult after synthesis by the latter approach.

6,13-Dicyanopentacene can be obtained from 6,13-pentacenequinone at lower temperatures when using LiCN as the catalyst. Single crystals of this compound (and three other target molecules) were obtained by solvent evaporation. X-ray diffrac-

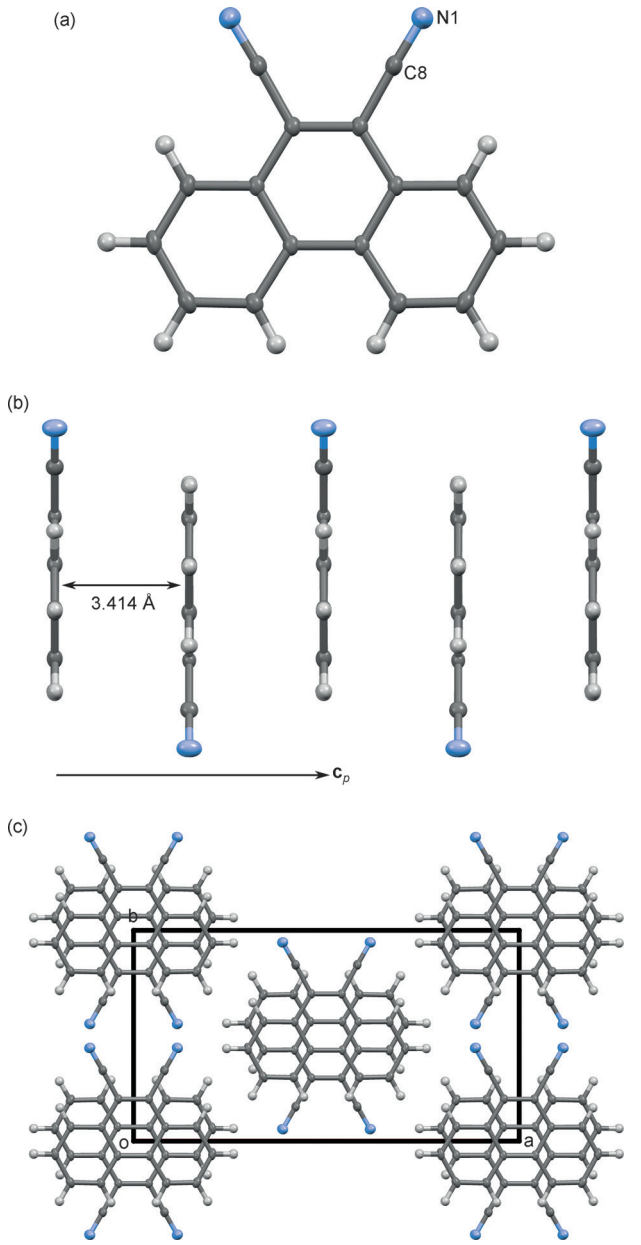


Figure 4. a) Molecular structure, b) rods of π-stacked molecules, and c) packing of 9,10-dicyanophenanthrene **15** viewed down [001]. Atom designations as in Figure 1.

tion revealed a crystal structure promising for OFET applications.

Furthermore, conversion of *ortho*-quinones to cyanoarenes is possible by following the same protocol as for the conversion of the *para*-quinones.

Experimental Section

Experimental and instrumental details for the synthesis and characterization of all compounds are provided in the Supporting Information.

General procedure for the synthesis of readily soluble cyanoarenes (3 a, 3 b, 9, 12, 17)

Starting material (1.00 equiv) and KCN (0.05 equiv) were suspended/dissolved in dry DMF (0.5 mL mmol^{-1} starting material) in a sealed reaction vial equipped with a septum. TMSCN (2.05 equiv) was added dropwise and the resulting mixture stirred at room temperature until full conversion to the cyanohydrin intermediate. The reaction was then diluted with dry MeCN (3.0 mL mmol^{-1} starting material). PBr_3 (1.20 equiv) was added in one portion and the vial was heated to 50 °C until full conversion of the intermediate occurred. The reaction was then allowed to cool to room temperature and CH_2Cl_2 (about 8 mL mmol^{-1} starting material) was added. Direct filtration over a thick pad of silica (conditioned with CH_2Cl_2 and some drops of MeCN) with CH_2Cl_2 as the eluent afforded the pure product after evaporation of the solvent.

General procedure for the synthesis of weakly soluble cyanoarenes (5 a, 5 b)

Starting material (1.00 equiv) and KCN (0.05 equiv) were mixed with dry DMF (0.5 mL mmol^{-1} starting material) in a sealed reaction vial equipped with a septum. TMSCN (2.05 equiv) was added dropwise to the slurry and the resulting mixture stirred at room temperature until full conversion to the cyanohydrin intermediate. The reaction was then diluted with dry MeCN (3.0 mL mmol^{-1} starting material). PBr_3 (1.20 equiv) was added in one portion and the vial was heated to 50 °C until full conversion of the intermediate occurred. The reaction was then allowed to cool to room temperature. MeCN (about 4 mL mmol^{-1} starting material) was added and stirring was stopped. After settling of the solid, the overlaying liquid was removed, replaced with fresh MeCN, and stirred again for 1 min. This was repeated another three times before the solid was filtered off and washed once with MeCN. Trituration in boiling toluene (50 mL mmol^{-1} starting material) and subsequent filtration afforded the pure product.

Procedure for the synthesis of larger cyanoarenes (15)

n-Butyllithium (0.10 equiv, 2.5 M in hexanes) was added to rigorously stirred TMSCN (2.20 equiv) in a sealed reaction vial equipped with a septum under an argon atmosphere at room temperature. After 15 min, the resulting suspension was added dropwise to a second reaction vial, equipped with a septum under an argon atmosphere, charged with 6,13-pentacenequinone **14** and precooled to 0 °C. Dry DMF (0.5 mL mmol^{-1} starting material) was used to fully transfer the residues of the suspension. The resulting mixture was stirred at 0 °C until full conversion to the cyanohydrin intermediate occurred. After 6 h, the reaction was diluted with dry CH_2Cl_2 (3.0 mL mmol^{-1} starting material). PBr_3 (1.20 equiv) was added in one portion and the reaction stirred overnight, still kept at 0 °C. Solvents and volatile side products were then evaporated in vacuo and the residue was purified by column chromatography (PE/CH_2Cl_2, gradient from 40% to 70% CH_2Cl_2) to afford 6,13-dicyanopentacene **15** as a pure dark solid.

CCDC 1443832–1443835 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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