Multistep Redox Systems, LXV[1]

Tethered 1,4-Benzoquinones and Their DCNQI Derivatives: Syntheses, Electronic Interactions, Redox Properties, Charge-Transfer Complexes, and Copper Salts

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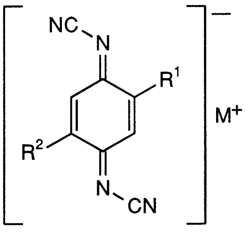
Bisquinones **16**–**20**, in which the quinoid moieties are tethered by 2–6 methylene units, have been synthesized via the bis(dimethoxybenzenes) **2**, **6**, **9**, **14**, and **15**. Compounds **16**–**20** were transformed into the corresponding bis(DCNQIs) **21**–**25** using standard procedures. Interactions between the two quinoid units, which fade with the length of the tethering chain, have been observed by ^{13}C-NMR spectroscopy, backed by calculated charge densities (Table 1) and by their cyclovoltammograms which indicate two independent two-step electron transfers. Similar results arise from ESR investigations of the bis(quinone) radical ions. All DCNQIs **21**–**25** form charge-transfer complexes with TTF and copper radical anion salts with reasonable powder conductivities. Since single crystals could not be grown, the structure of these materials remains unknown.

DCNQIs are valuable acceptors for highly conducting charge-transfer (CT) complexes and especially for radical anion salts of type **A** derived from 2,5-disubstituted DCNQIs.[3] In salts of type **A** the metal ions are arranged like strings of pearls surrounded by stacks of DCNQI ligands which connect the metal ions.



M = Li, Na, K, NH_4
Rb, Tl, Ag, Cu

R^1,R^2 = MeO, Me, Cl, Br, I

Space groups: $I4_1/a$; C2/c; P4/n

Type **A**

All belong to the space group $I4_1/a$ or the closely related $C2/c$ and $P4/n$.[4] Furthermore, these DCNQI copper salts show high metallic conductivities, even down to low temperatures.[3]

We therefore asked the question if these unique solid-state properties may be reinforced or turned into different ones by tethering together two DCNQI molecules with two to six methylene groups.[5] Depending on the length of this tether, the connection between two DCNQI moieties may occur either in one stack or between two neighbouring stacks (folded or stretched conformations, respectively).

We now present the syntheses and some properties of bis(quinones) **16**−**20** and the corresponding bis(DCNQIs) **21**−**25** in which the quinoid moieties are tethered by two to six methylene units. From **21**−**25** CT complexes with TTF and copper radical anion salts were obtained with reasonable conductivity. However, since no single crystals could be grown, the structure of these new organic conductors remains unknown.

It should be mentioned here that the properties of tethered TTF units have already been studied by several groups.[6]

Syntheses of Tethered 1,4-Benzoquinones and DCNQIs[7]

In all cases appropriate substituted 1,4-dimethoxybenzenes served as starting materials.

Tether $(CH_2)_2$

By reductive coupling of the chloromethylated starting material **1** the 1,2-bis(2,5-dimethoxyphenyl)ethanes **2a**[8] and **2b**[9] have already been synthesized.[10]

Tether $(CH_2)_3$

Products **6a**, **b** and **d** are easily available along the route **3** + **4** → **5** → **6** which has been described for **6a** (R^1, R^2 = H).[11] Bromination transforms **6a** and **6d** smoothly into **6c** and **6e**, respectively.

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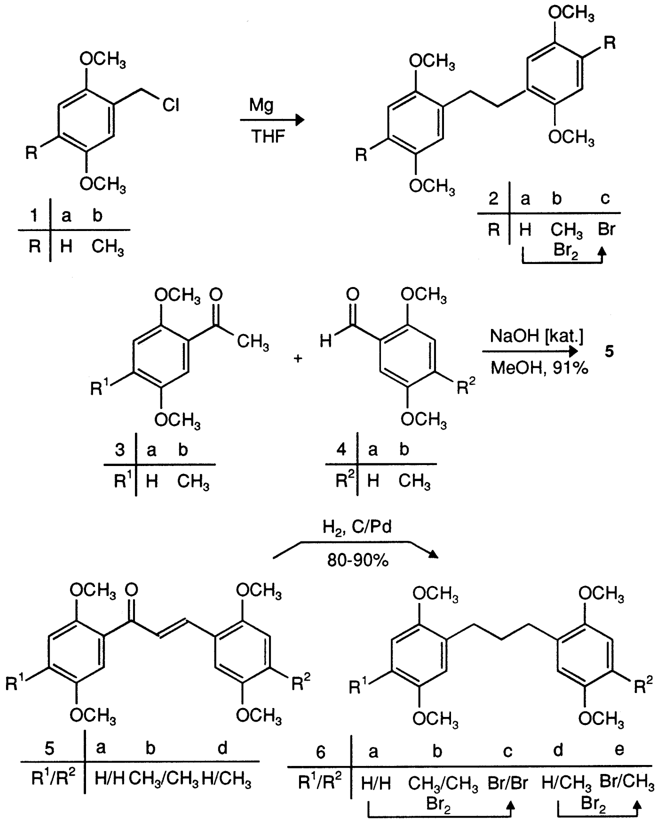
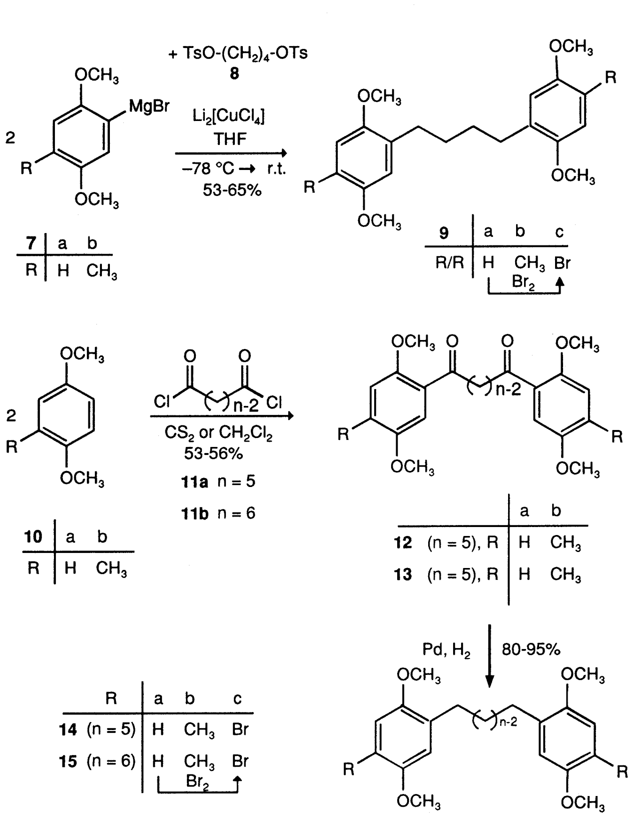
Scheme 1



Scheme 2



Tether $(CH_2)_4$

Introduction of a C_4 unit by succinic acid dichloride is not advisable, since this Friedel-Crafts acylation is known to yield mostly 5,5-diarylfuranones instead of 1,4-diarylbutane-1,4-diones.[12] However, direct introduction of the $(CH_2)_4$ unit via butane-1,4-diol ditosylate (**8**) and the appropriate aromatic Grignard reagents **7** afforded directly **9a, b** in good yields if the reaction was performed in the presence of catalytic amounts of lithium tetrachlorocuprate.[13] Again, the dibromo derivative **9c** was easily obtained from **9a** by bromination (Scheme 2).

Tethers $(CH_2)_5$, $(CH_2)_6$

With both the dichlorides of glutaric acid (**11a**) and adipic acid (**11b**) the Friedel-Crafts route with **10** smoothly yielded the pentamethylene and hexamethylene tethers in **14** and **15**, respectively, via the diketones **12** and **13** after catalytic reduction (Scheme 2).

Quinones and DCNQIs

After introduction of the tethering chains, the products were demethylated by boron tribromide and oxidized to the corresponding bis(quinones) **16**−**20**. These were transformed into the bis(DCNQIs) **22**−**25** by the well-established reagent bis(trimethylsilyl)carbodiimide/titanium tetrachloride[3][14] (Scheme 3) . Probably as a result of their low solubilities, lower yields of **22**−**25** were observed compared to mono(DCNQIs).[14] The very low solubilities of **16** prevented isolation of pure **21**.

Chainlength-Dependent Electronic Effects between the Aromatic (16−20) and Quinoid (21−25) Moieties

For the purpose outlined above, information about possible folded or streched conformations of the bis(quinones) **16**−**21** and bis(DCNQIs) **21**−**26** is of primary importance. The existence of two possible conformations means that it is not obvious that the effect of the quinoid moieties on each other will continuously fade away with the length of the tether.

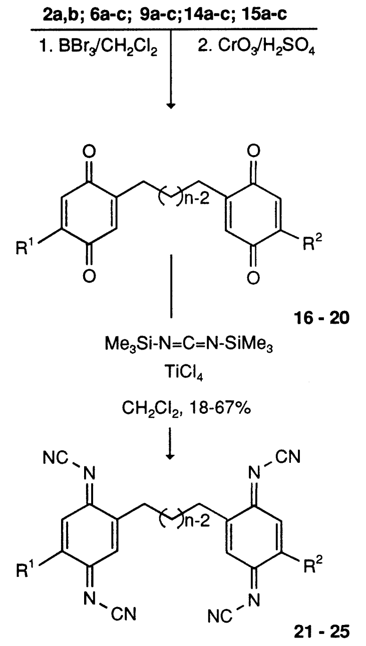
^{13}C-NMR Shifts and Charge Densities

The sensitivity of aromatic ^{13}C-NMR shifts towards the chain lengths of alkyl substituents is well documented,[15][16] together with their correlation with calculated charge densities.[17]

For comparison, the limiting case should be compounds in which the end groups are separated by an infinite ($n = \infty$) number of methylene groups. The dodecyl residue in **26** and **27** serves as a suitable approximation.[18]

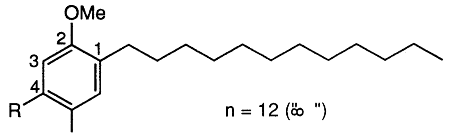
As seen from Figure 1, the polarizing effect of the two quinoid rings in **16**−**20** on each other increases with σ_p of the substituents in the 5-position ($CH_3 < H < Br$). Consequently, the gradients of the graphs increase in the same order.

Scheme 3

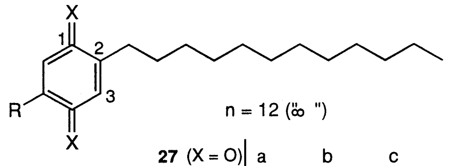


		R1 / R2 a	b	c	d	e
16	**21*** (n=2)	H/H	CH_3/CH_3	Br/Br	—	—
17	**22** (n=3)	H/H	CH_3/CH_3	Br/Br	H/CH_3	Br/CH_3
18	**23** (n=4)	H/H	CH_3/CH_3	Br/Br	—	—
19	**24** (n=5)	H/H	CH_3/CH_3	Br/Br	—	—
20	**25** (n=6)	H/H	CH_3/CH_3	Br/Br	—	—

*not obtained in pure state



26	a	b	c
R	H	CH_3	Br
Δδ (C_1-C_4) ^{13}C NMR	22.5	5.0	23.5



27 (X = O)	a	b	c
R	H	CH_3	Br
Δδ (C_2-C_3) ^{13}C NMR	17.4	17.3	18.7

28 (X = N–CN)

Figure 1. Correlation as in Figure 2 but with α,ω-bis(5-methyl-1,4-benzoquinon-2-yl)alkanes **16**–**20**. ····· marks the data for **27** (→ $n = \infty$)

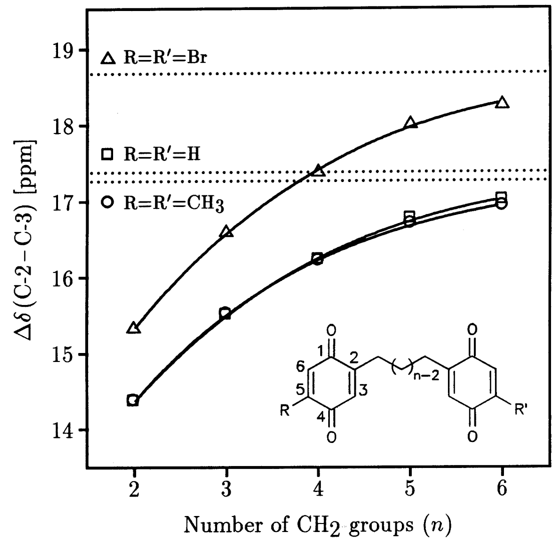
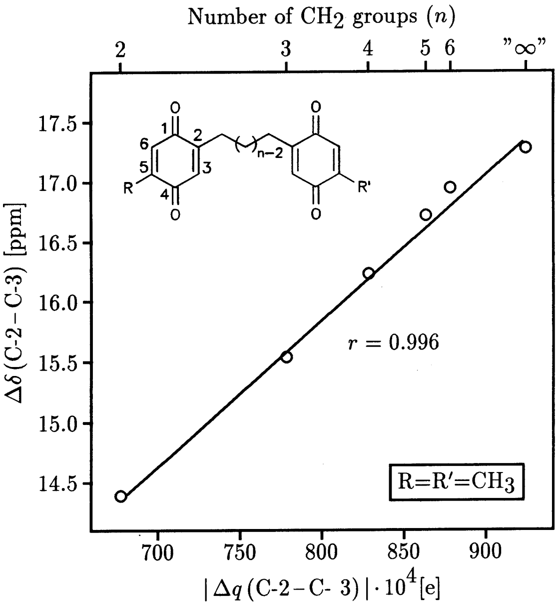


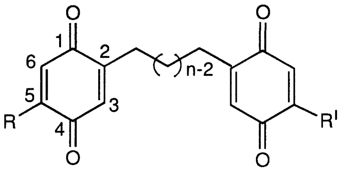
Figure 2. Correlation of the differences of the chemical shifts of ^{13}C-NMR signals Δδ (C-2 – C-3) with the differences between calculated (AM1) partial charges |Δq (C-2 – C-3)| in α,ω-bis(5-methyl-1,4-benzoquinon-2-yl)alkanes **16**–**20**



Since definite correlations between ^{13}C-NMR shifts and calculated charge densities have been found for several examples[17], we calculated the charge densities of tethered quinones **16b**–**20b** with the semiempirical program AM1. As starting geometries, we chose structures with an all-*anti* conformation of the alkyl bridges which were preoptimized by the molecular mechanics program *PCMODEL*. The resulting structures represent *local* energy minima (not necessarily *global* minima). The partial charges q at C-2 and C-3 together with their difference Δq are summarised in Table 1.

By shortening the tether, (negative) charge density is increased at C-2, whereas q at C-3 is diminished. With $n = 6$ (**20b**) these values approach closely those of **27b**, a model for $n = \infty$. Moreover, there exists an excellent linear correlation (0.996) between these calculated differences Δq (C-2 – C-3) and the measured ^{13}C-NMR shift differences Δδ (C-

Table 1. Calculated (AM1) negative partial charges q(C-2), q(C-3), and differences Δq (C-2 − C-3) of α,ω-bis(5-methyl-1,4-benzoquinon-2-yl)alkanes **16b**−**20b** with varying length of the alkyl bridges



	16b	**17b**	**18b**	**19b**	**20b**	**27b**
n	2	3	4	5	6	∞
q(C-2) × 10^4	1021	977	960	942	936	913
q(C-3) × 10^4	1699	1756	1789	1806	1815	1838
$\lvert\Delta q\rvert$ × 10^4	678	779	829	864	879	925

2 − C-3) (Figure 2).The clear correlation of Figure 2 and the smooth slope of the graphs in Figure 1 indicate that bis(quinones) **16**−**20** definitely prefer a streched all-*anti* conformation in solution.

The bis(DCNQIs) **21**−**25** are supposed to behave in the same way. However, ^{13}C-NMR investigations were not possible due to their very low solubilities.

Cyclovoltammograms

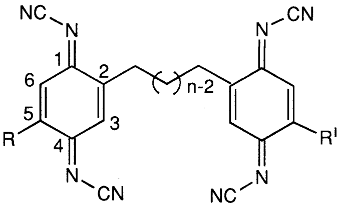
Intramolecular interactions between the end groups in bis(quinones) **16**−**20** and bis(DCNQIs) **22**−**25** are also expected to influence their redox potentials. In Table 2 potentials E_2 and E_1 are summarised for the twelve bis(DCNQIs) **22a, b, c**−**25a, b, c** together with those of **28a, b, c**[18] for comparison ($n = \infty$). Average potentials are given since for the shortest systems **22** ($n = 3$) two potentials E_2 and E_1 were observed with a separation of ca. 40−80 mV; this is a clear indication of Coulomb interactions.

According to a theoretical analysis, electron-transfer reactions with compounds containing several identical redox moieties without interactions should produce cyclovoltammograms of the same shape as monomeric ones.[19] Moreover, given ideal reversibility, the difference between the two peak potentials E_{pc} and E_{pa} should amount to 59 mV (25°C). But even with monomolecular DCNQIs, and also with **28a**, **c** this difference was found to be around 80−90 mV. However, with the bimolecular DCNQIs **22**−**25** this difference amounts to 130−155 mV for $n = 3$ and approaches the value of **28** with increasing length of the tethering chain (n = 4, 5, 6) (Table 2).

Such an enlarged ΔE_p has mainly been taken to be due to electronic interactions between the redox centers, although slow electron transfer, strong conformational changes and adsorption of the products would produce very similar results.

The latter phenomena can be excluded at least for **27a**−**27c** ($n = 3$) with the largest peak separations ΔE_p. According to Table 2 all bromo-substituted bis(DCNQIs) (**22c**−**25c**) are reduced more easily than the methyl-substituted counterparts (**22a**−**25a**) by ca. 200 mV. The mixed derivative (CH_3/Br) **22c** consequently shows four clearly separated redox waves according to four reduction potentials $E_2'' = -0.44$ V, $E_2' = 0.23$ V, $E_1'' = -0.19$ V, and $E_1' = -0.42$ V with the normal separation of the peak potentials, namely 80 mV and 90 mV, respectively, in accord with **28**. Also the diferences between the potentials E_2 and E_1 in **22c**, $E_2'' - E_1''$ = 660 mV (Br-DCNQI) and $E_2'' - E_1'$ = 650 mV (Me-DCNQI) are as large as in **22a**−**c**.

Table 2. Average[a] redox potentials $E_2(\varnothing)$ and $E_1(\varnothing)$ of bis(DCNQIs) **22**−**25** and mono(DCNQI) **28**[b] for comparison determined by CV (CH_2Cl_2, Bu_4NBF_4, Pt vs. Ag/AgCl in CH_3CN); ΔEp difference of the peak potentials



	n	R = R′	$E_2(\varnothing)$ [V]	ΔE_p [mV]	$E_1(\varnothing)$ [V]	ΔE_p [mV]	$E_2 - E_1$ [mV]
22b	3	CH_3	0.25	140	−0.39	150	635
23b	4	CH_3	0.24	105	−0.39	140	625
24b	5	CH_3	0.22	100	−0.40	130	620
25b	6	CH_3	0.23	95	−0.38	115	610
28b	∞	CH_3	0.22	80	−0.38	85	600
22a	3	H	0.33	130	−0.33	150	655
23a	4	H	0.32	105	−0.32	140	640
24a	5	H	0.31	95	−0.32	115	630
25a	6	H	0.32	90	−0.30	110	620
28e	∞	H	0.30	80	−0.32	85	620
22c	3	Br	0.47	155	−0.19	140	655
23c	4	Br	0.45	105	−0.17	140	620
24c	5	Br	0.45	95	−0.18	110	625
25c	6	Br	0.45	95	−0.18	110	625
28c	∞	Br	0.43	95	−0.20	95	630

[a] For $n = 3$ two potentials are observed for both E_2 and E_1 with differences of ca. 40−80 mV.[7] – [b] Mono(DCNQI) **28** is derived from **27**[18]

These results indicate that the large peak separations ΔE_p in **22a**−**c** are mainly caused by electrostatic interactions of the two tethered redox units. As is to be expected, these effects disappear with increasing n.

The constancy of E_2 and E_1 (or E_m, respectively) within the series **22a**, **b**, **c** to **25a**, **b**, **c** is again in accord with a stretched conformation and [with the possible exception of $n = 3$ (see below)] eliminates the possibility of intramolecular pimerisation[22] for a certain length of the tether.

ESR Investigations

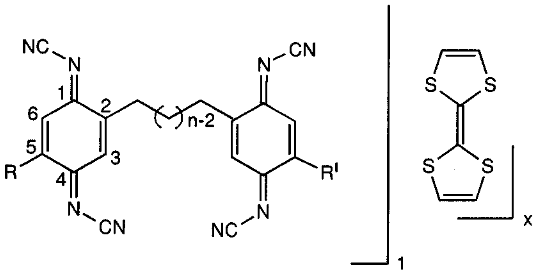
The results of R. Gerson and P. Felder[20] with bis(quinones) **16**−**20** (n = 2−6) will be discussed briefly. ESR signals of all mono- and trianions indicate the single electron to be delocalized only over one of the two quinone units. Both mono- and trianions with $n > 4$ show the hyperfine structure expected for their monomeric counterparts. With $n = 2$ the different ESR pattern is attributed to diminished motion of the end groups and Coulomb interaction. With $n = 3$, a second species is derived from the ESR data which has not yet been identified. Intramolecular pimerization may possibly take place which is well known for bis(pyridinyl) radicals linked by a trimethylene chain.[22]

From matrix experiments on dianions the distances of the two quinone moieties (center) could be estimated to be 650 pm ($n = 2$), 720 pm ($n = 3$), 840 pm ($n = 4$), 970 pm ($n = 5$), and 850 pm ($n = 6$). These data agree quite well with the distances calculated for the bis(quinones) (vide supra): 660 pm ($n = 2$), 740 pm ($n = 3$), 900 pm ($n = 4$), 990 pm ($n = 5$). Only the calculated distance for $n = 6$ (1140 pm) differs significantly from that obtained from the ESR data, obviously suggesting a coiled conformation for the corresponding dianion.

CT Complexes with TTF[7]

Combining solutions of TTF and **22a**−**22c** in acetonitrile yielded dark green solutions from which the CT complexes precipitated as dark powders on cooling. With **22b**−**25b** the same procedure yielded green solutions again. However, on cooling only the starting bis(quinones) precipitated, probably due to their low solubility and weak acceptor properties ($E_2 \approx 0.23$ V, see Table 2). With **22c**−**25c** dichloromethane/acetonitrile must be applied. The much less soluble CT complex precipitated without cooling, mostly as a microcrystalline material. The isolated CT complexes are summarised in Table 3. They prefer to adopt stochiometries close to 1:2 in accord with the 1:1 stochiometry for many monomolecular DCNQIs.[21]

Table 3. CT complexes from bis(DCNQIs) **22**−**25** (n = 3−6) and TTF; stoichiometries and powder conductivities (σ_p)



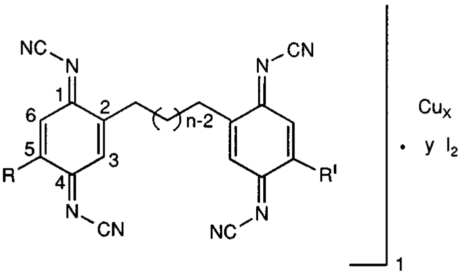
DCNQI	R	R′	n	x	σ_p [S cm^{-1}]
22a	H	H	3	2.0	8×10^{-3}
23a	H	H	4	2.8	4×10^{-2}
24a	H	H	5	2.5	8×10^{-3}
25a	H	H	6	1.9	1×10^{-4}
22c	Br	Br	3	2.0	1×10^{-2}
23c	Br	Br	4	2.0	3×10^{-4}
24c	Br	Br	5	2.2	4×10^{-5}
25c	Br	Br	6	2.0	5×10^{-5}

Powder conductivities of these CT complexes are found between 10^{-2} and 10^{-5} S cm^{-1}, the normal range for DCNQI/TTF complexes.[21]

Bis(DCNQI) Copper Salts[7]

On adding solutions of copper(I) iodide in acetonitrile to solutions of the bis(DCNQIs) in acetonitrile(/dichloromethane) black amorphous precipitates were immediately formed. Also, the rather general procedure of immersing a clean copper wire in solutions of DCNQIs in acetonitrile[3][22] does not yield crystalline radical anion salts. As demonstrated with **22b** the wire becomes covered with a black amorphous layer within a few hours and further precipitation ceases after one day, obviously due to the low conductivity of the dark material. Its IR spectrum coincides with that of the precipitate obtained with copper(I) iodide. As is to be seen from Table 4, the stoichiometries of bis(DCNQI)/Cu salts are mostly close to 1:2. This means a 1:1 stoichiometry per DCNQI unit. So far, these relations have only been observed with voluminous 2,5-substituents[23][24] or with higher substituted DCNQIs[25] together with low conductivities, in sharp contrast to the highly conducting normal 2:1 DCNQI copper salts.[4]

Table 4. Copper radical anions salts from bis(DCNQIs) **22**−**25** (n = 3−6) and copper(I) iodide; stochiometries and powder conductivities (σ_p)



DCNQI	R	R′	n	x	y	σ_p [S cm^{-1}]
22a	H	H	3	2.0	−	5×10^{-5}
23a	H	H	4	1.8	0.2	3×10^{-5}
24a	H	H	5	1.6	0.2	9×10^{-5}
25a	H	H	6	1.8	0.2	1×10^{-3}
22b	CH_3	CH_3	3	1.9	−	8×10^{-3}
23b	CH_3	CH_3	4	1.8	0.2	4×10^{-2}
24b	CH_3	CH_3	5	1.8	0.6	1×10^{-1}
25b	CH_3	CH_3	6	not obtained		
22d	H	CH_3	3	1.7	0.3	8×10^{-3}
22e	Br	CH_3	3	1.7	0.3	8×10^{-3}
22c	Br	Br	3	1.8	−	3×10^{-5}
23c	Br	Br	4	1.0	0.2	1×10^{-3}
24c	Br	Br	5	1.8	0.2	1×10^{-6}
25c	Br	Br	6	1.6	0.1	9×10^{-4}

It is therefore not surprising that most powder conductivities of the new copper salts are found in the range of 10^{-1} to 10^{-5} S cm^{-1}. Interestingly, iodine is found in the majority of these salts. On the assumption that iodine is incorporated as copper(I) iodide, then for these salts the stoichiometries bis(DCNQI)/Cu are close to 1:1.4−1.6, with **22a** and **22b** even 1:1.9 and 1:2, respectively.

Conclusion

Our ultimate goal, structure determination of both **21**−**25**/TTF complexes and **21**−**25** copper salts could not be realised due to the amorphous or microcrystalline character of these materials. Their conductivities range from below to within those of normal DCNQI/TTF complexes and copper radical anion salts. A specific positive effect of any tethered bis(DCNQI) is not observed. Nevertheless this new class of acceptors displays some interesting interactions between the two quinoid units, fading with the length of the tether which obviously prefers to adopt a stretched conformation. The different approaches for tethers with two to six methylene groups may be useful for other quinoid materials.

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Experimental Section

General: Apparatus, solvents etc. see part LXIV[1].

1,2-Bis(4-bromo-2,5-dimethoxyphenyl)ethane (**2c**): Procedure see **6c**. **2a** (5.29 g, 17.5 mmol), bromine (5.88 g, 36.8 mmol). The crude product was crystallized from ethanol (150 ml). Colorless crystals (7.29 g, 91%) of **2c**, m.p. 122−123°C. − IR (KBr): ṽ = 3000 cm^{-1}, 2940, 2850, 2830 (CH), 1490 (C=C). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.82 (s, 4 H, −CH$_2$−CH$_2$−), 3.76 (s, 12 H, −OCH$_3$), 6.57 (s, 2 H, 6-H), 7.01 (s, 2 H, 3-H). − ^{13}C NMR (50.3 MHz, CDCl$_3$):δ = 30.38 (t, −CH$_2$−CH$_2$−), 56.12, 56.94 (2q, −OCH$_3$), 108.55 (s, C-4), 114.74 (d, C-6), 115.65 (d, C-3), 130.44 (s, C-1), 149.73 (s, C-2), 152.00 (s, C-5). − $C_{18}H_{20}Br_2O_4$ (460.2): calcd. C 46.98, H 4.38; found C 47.18, H 4.42.

3-(2′,5′-Dimethoxy-4′-methylphenyl)-1-(2,5-dimethoxyphenyl)-2-propenone (**5d**): By adaptation of ref.[26] 2,5-dimethoxyacetophenone (10.8 g, 60.0 mmol) and 2,5-dimethoxy-4-methylbenzaldehyde (10.8 g, 60.0 mmol) in methanol (60 ml) were refluxed together with ca. 5 g of sodium hydroxide for 5 h. The product precipitated from the orange solution on cooling. After filtering and washing with a small amount of methanol, bright orange crystals of **5d** (18.6 g, 91%, m.p. 101−102°C) were isolated. − IR (KBr):ṽ = 3100 cm^{-1}, 2930, 2815 (CH), 1640 (C=O), 1600, 1570, 1500, 1490 (C=C). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.24 (s, 3 H, −CH$_3$), 3.79, 3.81, 3.83 (3 s, 12 H, −OCH$_3$), 6.73 (s, 1 H, 3′-H), 6.92 (d, *J* = 9.0 Hz, 1 H, 3-H), 7.00 (dd, *J* = 9.0, 3.0 Hz, 1 H, 4-H), 7.01 (s, 1 H, 6′-H), 7.16 (d, *J* = 3.0 Hz, 1 H, 6-H), 7.38 (d, *J* = 16.0 Hz, 1 H, −CO−C*H*=CH−), 7.93 (d, *J* = 16.0 Hz, 1 H, −CO−CH=C*H*). − ^{13}C NMR (63 MHz, CDCl$_3$): δ = 16.74 (q, −CH$_3$), 55.81, 56.12, 56.48 (3 q, −OCH$_3$), 109.74 (d, C-6′), 113.46, 114.45, 114.53 (3 d, C-3, -3′, -6), 118.47, d,C-4), 121.65 (d, C-1′), 126.40 (d, −CO−CH=CH−), 130.20, 131.30 (2 s, C-1, -4′), 139.40 (d, −CO−CH=CH−), 151.77, 152.31, 153.04, 153.57 (4 s, C-2, -2′, -5, -5′). − $C_{20}H_{22}O_5$ (342.4): calcd. C 70.16, H 6.48; found C 70.24, H 6.29.

1-(2,5-Dimethoxy-4-methylphenyl)-3-(2′,5′-dimethoxyphenyl)-propane (**6d**): By adaptation of ref.[27] a suspension of **5d** (17.1 g, 50.0 mmol) and 0.5 g Pd/C (10% Pd) in ethanol (100 ml) was hydrogenated at 40°C and 4 bar until the mixture became colorless. After addition of *p*-toluolsulfonic acid (0.2 g), hydrogenation was continued until no more hydrogen was consumed. The hot (ca. 80°C) solution was filtered through a pad of Celite®. From the cooled solution **6d** (13.4 g, 81%, m.p. 88−89°C) was isolated as colorless plates. − IR (KBr): ṽ = 3030 cm^{-1}, 2990, 2940, 2920, 2810 (CH), 1500 (C=C), 1220, 1210, 1045 (C−O). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.88 (quint, *J* = 7.8 Hz, 2 H, 8-H$_2$), 2.20 (s, 3 H, −CH$_3$), 2.65 (t, *J* = 7.8 Hz, 4 H, 7-H$_2$, 7′-H$_2$), 3.75, 3.76, 3.77 (3 s, 12 H, −OCH$_3$), 6.66 (s, 2 H, 3-, 6-H), 6.67 (dd, *J* = 8.7, 2.9 Hz, 1 H, 4′-H), 6.76 (d, *J* = 8.7 Hz, 1-, 3′-H), 6.77 (d, *J* = 2.9 Hz, 1 H, 6′-H). − ^{13}C NMR (63 MHz, CDCl$_3$): δ = 16.08 (q, −CH$_3$), 29.97 (t, C-8), 30.06, 30.16 (2 t, C-7, -7′), 55.62, 55.93, 56.11 (3 q, −OCH$_3$), 110.62 (d, C-4′), 111.18 (d, C-3′), 112.73 (d, C-6), 113.91 (d, C-3), 116.17 (d, C-6′), 124.31 (s,C-4), 128.84 (s, C-1), 132.35 (s, C-1′), 151.21 (s, C-2), 151.47, 151.83 (2 s, C-2′, -5′), 153.44 (s, C-5). − $C_{20}H_{26}O_4$ (330.5): calcd. C 72.70, H 7.93; found C 72.57, H 7.87.

1-(4-Bromo-2,5-dimethoxyphenyl)-3-(2′,5′-dimethoxy-4′-methylphenyl)propane (**6e**): A solution of bromine (3.02 g, 18.9 mmol) in acetic acid (20 ml) was slowly added to a suspension of **6d** (5.95 g, 18.0 mmol) in acetic acid (40 ml). After stirring for 1 h, the mixture was poured into ice-cold water (250 ml). The precipitate was filtered off, washed with a small amount of cold ethanol and dried. Sublimation (170°C/0.01 Torr) yielded pure **6c** (3.10 g, 42%) from the main fraction. From a second fraction (2.6 g) after flash chromatography (SiO$_2$, dichloromethane/petroleum ether (PE), 2:1; further **6c**, 1.50 g, 20%) was isolated. Colorless crystals (62%, m.p. 144−145°C). − IR (KBr): ṽ = 2990 cm^{-1}, 2945, 2920, 2840, 2820 (CH), 1500, 1485 (C=C), 1200, 1040 (C−O). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.85 (quint, *J* = 7.8 Hz, 2 H, 8-H$_2$), 2.20 (s, 3 H, −CH$_3$), 2.63 (t, *J* = 7.8 Hz, 4 H, 7-, 7′-H$_2$), 3.76, 3.78, 3.83 (3 s, 12 H, −OCH$_3$), 6.65 (s, 1 H, 6′-H), 6.67 (s, 1 H, 3′-H), 6.75 (s, 1 H, 6-H), 7.01 (s, 1 H, 3-H). − ^{13}C NMR (63 MHz, CDCl$_3$): δ = 16.09 (q, −CH$_3$), 29.95 (t, C-8), 30.02, 30.11 (2 t, C-7, -7′), 56.09, 56.12, 56.97 (3 q, −OCH$_3$), 108.20 (s, C-4), 112.76 (d, C-6′), 113.94 (d, C-3′), 114.41 (d, C-6), 115.70 (d, C-3), 124.49 (s C-4′), 128.59 (s,C-1′), 131.42 (s, C-1), 149.83 (s, C-2), 151.19, 151.51 (2 s, CD-2′, -5′), 152.01 (s, C-5). − $C_{20}H_{25}BrO_4$ (409.3): calcd. C 58.69, H 6.16, Br 19.52; found C 58.67, H 6.31, Br 19.53.

1,4-Bis(2,5-dimethoxyphenyl)butane (**9a**): By adaptation of ref.[13] from magnesium chips (5.47 g, 225 mmol) and 2-bromo-1,4-dimethoxybenzene in THF (100 ml) a Grignard reagent was prepared. After reflux for 1.5 h, a 0.1 M solution (5.00 ml, 500 μmol) of Li_2CuCl_4 in THF was added to the cooled solution (−10°C) and then 1,4-bis (*p*-toluolsulfonyloxy)butane[28] (35.9 g, 90.0 mmol) in THF (100ml) slowly introduced. After stirring for 90 h, the mixture was poured on ice (250 g) and concentrated HCl (20 ml). The product was extracted with diethyl ether (3 × 100 ml), the organic phase washed with saturated Na$_2$CO$_3$ solution, dried (Na$_2$SO$_4$) and the solvent evaporated. The residual orange oil was dissolved in hot methanol (50 ml) from which after cooling (40°C) **9a** (17.0 g) was isolated. From methanol, colorless crystals of **9a** (15.8 g, 53%, m.p. 69°C). − IR (KBr): ṽ = 3060 cm^{-1}, 2980, 2940, 2920, 2905, 28454, 2820 (CH), 1605, 1580, 1500 (C=C), 1220, 1210, 1050, 1020 (C−O). − ^{13}C NMR (250 MHz, CDCl$_3$): δ = 1.64 (tt, *J* = 7.0, 3.5 Hz, 4 H, 8-, 8′-H$_2$), 2.61 (t, *J* = 7.0 Hz, 4 H, 7-, 7′-H$_2$), 3.74, 3.76 (2 s, 12 H, −OCH$_3$), 6.66 (dd, *J* = *8*.7, 3.0 Hz, 2 H, 4-, 4′-H), 6.73 (d, *J* = 8.7 Hz, 2 H, 3-, 3′-H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 29.69 (C-8, -8′), 3.09 (C-7, -7′), 55.67, 56.01 (−OCH$_3$), 110.71 (C-4, -4′), 111.35 (C-3, -3′), 116.32 (C-6, -6′), 132.57 (C-1, -1′), 151.89 (C-2, -2′), 153.52 (C-5, -5′). − $C_{20}H_{26}O_4$ (330.4): calcd. C 72.70, H 7.93; found C 72.78, H 8.09.

1,4-Bis(2,5-dimethoxy-4-methylphenyl)butane (**9b**)*:* Procedure cf. **9a**. Magnesium chips (1.28 g, 52.5 mmol), 2-bromo-1,4-dimethoxy-5-methylbenzene (11.6 g, 50.0 mol), THF (50 ml), reflux (2 h). At −78°C addition of Li_2CuCl_4 in THF 1 M (1 ml, 100 μmol) and 1,4-bis(*p*-toluolsulfonyloxy)butane[25] inTHF (30 ml), 16 h at room temp. The mixture was poured into ice-cold water (200 ml) and concentrated HCl (20 ml). The isolated precipitate was washed with some cold methanol and dried. Sublimation (ca. 160°, 0.01 Torr) of the crude product (5.41 g) yielded **9b** (4.68 g, 65%) as colorless crystals, m.p. 161°C. − IR (KBr): ṽ = 3000 cm^{-1}, 2945, 2925, 2860, 2820 (CH), 1500 (C=C), 1205, 1040 (C−O). − ^{1}H NMR

(200 MHz, $CDCl_3$): δ = 1.64 (tt, *J* = 6.6, 3.3 Hz, 4 H, H-, 8′-H_2), 2.20 (s, 6 H, $-CH_3$), 2.61 (t, *J* = 7.0 Hz, 4 H, 7-, 7′-H_2), 3.76, 3.77 (2 s, 12 H, $-OCH_3$), 6.64 (s, 2 H, 6-, 6′-H), 6.66 (s, 2 H, 3-, 3′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.11 ($-CH_3$), 30.05 (C-8, -8′), 30.21 (C-7, -7′), 56.16, 56.25 ($-OCH_3$), 112.94 (C-6, -6′), 114.07 (C-3, -3′), 124.35 (C-4, -4′), 129.23 (C-1, -1′), 151.25, 151.58 (C-2, -2′, -5, -5′). − $C_{22}H_{30}O_4$ (358.5): calcd. C 73.71, H 8.43; found C 73.77, H 8.36.

1,4-Bis(4-bromo-2,5-dimethoxyphenyl)butane (**9c**): Procedure cf. **6c**. Suspension of **9a** (6.61 g, 20.0 mmol), acetic acid (40ml), bromine (6.71 g, 42.0 mmol) in acetic acid (20 ml), 45 min. Sublimation (180°C/0.01 Torr) of the crude product (8.96 g) yielded **9c** (8.28 g, 86%) as colorless crystals, m.p. 164−165°C. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2950, 2930, 2900, 2860, 2830 (CH), 1490 (C=C), 1210, 1050, 1040 (C−O). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 1.60 (tt, *J* = 6.6, 3.3 Hz, 4 H, 8-, 8′-H_2), 2.59 (t, *J* = 7.0 Hz, 4 H, 7-, 7′-H_2), 3.76, 3.82 (2 s, 12 H, $-OCH_3$), 6.72 (s, 2 H, 6-, 6′-H), 7.01 (s, 2 H, 3-, 3′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.11 ($-CH_3$), 29.54 (C-8, -8′), 30.05 (C-7, -7′), 56.14, 57.04 ($-OCH_3$), 108.37 (C-4, -4′), 114.61 (C-6, -6′), 115.86 (C-3, -3′), 131.44 (C-1, -1′), 149.91 (C-2, -2′), 152.03 (C-5, -5′). − $C_{20}H_{24}Br_2O_4$ (488.2): calcd. C 49.12, H 4.95, Br 32.73; found C 49.08, H 4.93, Br 32.75.

1,5-Bis(2,5-dimethoxyphenyl)pentane (**14a**)*:* The compound was prepared according to ref.[27]. **14a** (74%, m.p. 46−47°C, ref.[27]: 57%, m.p. 47−48°C). − IR (KBr):$\tilde{\nu}$ = 2980 cm^{-1}, 2920, 2845, 2820 (CH), 1600, 1580, 1495 (C=C), 1215, 1045, 1020 (C−O). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44 (m, 2 H, 9-H_2), 1.61 (m, 4 H, 8-, 8′-H_2), 2.58 (t, *J* = 7.0 Hz, 4 H, 7-, 7′-H_2), 3.74, 3.76 (2 s, 12 H, $-OCH_3$), 6.66 (dd, *J* = 8.6, 3.0 Hz, 2 H, 4-, 4′-H), 6.73 (d, *J* = 3.0 Hz, 2 H, 6-,6′-H), 6.75 (d, *J* = 8.6 Hz, 2 H, 3-, 3′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.48 (C-9), 29.79 (C-8, -8′), 30.21 (C-7, -7′), 55.59, 56.92 ($-OCH_3$), 110.56 (C-4, -4′), 111.19 (C-3, -3′), 116.26 (C-6, -6′), 132.63 (C-1, -1′), 151.80 (C-2, -2′), 153.43 (C-5, -5′).

1,5-Bis(2,5-dimethoxy-4-methylphenyl)pentane (**14b**): By adaptation of ref.[27] 2,5-dimethoxytoluene (38.0 g, 250 mmol) was added at 0°C to a suspension of aluminium trichloride (36.0 g, 270 mmol) in CS_2 (200 ml). To this mixture glutaric acid dichloride (21.1 g, 125 mmol) in CS_2 (75 ml) was slowly added. The mixture became dark and solidified. After 16 h at room temp., the reaction was quenched with ice (250 mg) and conc. HCl (30 ml). The product was extracted with diethyl ether (300 ml), washed neutral ($NaHCO_3$) and dried ($MgSO_4$). After concentration, 1,5-bis(2,5-dimethoxy-4-methylphenyl)pentane-1,5-dione (**12b**, 25.1 g, 50%) remained as colorless needles, m.p. 156°C. A suspension of **12b** (24.0 g, 60.0 mmol) and 0.5 g Pd/C (10% Pd) in acetic acid (100 ml) was hydrogenated at 80°C. The filtered solution was poured into ice-cold water (600 ml) and stirred for 30 min. The isolated precipitate was washed with some water and cold methanol and dried. Recrystallization of the crude product (21.8 g) from methanol (250ml) afforded **14b** (20.6 g, 93%) as colorless plates, m.p. 72°C. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2990, 2945, 2920, 2845, 2820 (CH), 1505 (C=C), 1205, 1040 (C−O). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43 (m, 2 H, 9-H_2), 1.59 (m, 4 H, 8-, 8′-H_2), 2.20 (s, $-CH_3$), 2.57 (t, *J* = 7.3 Hz, 4 H, 7-, 7′-H_2), 3.76, 3.77 (2 s, 12 H, $-OCH_3$), 6.64 (s, 2 H, 6-, 6′-H), 6.66 (s, 2 H, 3-, 3′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.05 ($-CH_3$), 29.60 (C-9), 30.17 (C-8, -8′), 30.27 (C-7, -7′), 56.16, 56.22 ($-OCH_3$), 112.98 (C-6, -6′), 114.10 (C-3, -3′), 124.38 (C-4, -4′), 129.35 (C-1, -1′), 151.27. 151.60 (C-2, -2′, -5, -5′). − $C_{23}H_{32}O_4$ (372.5): calcd. C 74.16, H 8.66; found C 74.70, H 8.72.

1,5-Bis(4-bromo-2,5-dimethoxyphenyl)pentane (**14c**): Bromine (6.71 g, 42.0 mmol) in acetic acid (20 ml) was slowly added to a suspension of **14a** (6.39 g, 20.0 mmol) in acetic acid (40 ml). Further procedure see **9c**. Sublimation (160°C/0.8 Torr) yielded **14c** (7.80 g, 78%) as colorless crystals, m.p. 102−103°C. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2920, 2830 (CH), 1570, 1490 (C=C), 1205, 1050, 1030 (C−O). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39 (m, 2 H, 9-H_2), 1.57 (m, 4 H, 8-, 8′-H_2), 2.55 (t, *J* = 7.4 Hz, 4 H, 7-, 7′-H_2), 3.76, 3.83 (2 s, 12 H, $-OCH_3$), 6.72 (s, 2 H, 6-H, -6′-H), 7.01 (s, 2 H, 3-, 3′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.27 (C-9), 29.72 (C-8, -8′), 30.21 (C-7, -7′), 56.13, 57.03 ($-OCH_3$), 108.35 (C-4, -4′), 114.62 (C-6, -6′), 115.86 (C-3, -3′), 131.63 (C-1, -1′), 149.94 (C-2, -2′), 152.03 (C-5, -5′). − $C_{21}H_{26}Br_2O_4$ (502.2): calcd. C 50.22, H 5.22; found C 50.70, H 5.27.

1,6-Bis(2,5-dimethoxyphenyl)hexane (**15a**): A suspension of **13a**[27] (17.6 g, 14.5 mmol) and Pd/C (10% Pd, 0.5 g) in acetic acid (100 ml) was hydrogenated. Procedure see **14b**. Recrystallization of the crude product (13.1 g) from methanol (100 ml) afforded **15a** (12.4 g, 78%) colorless crystals, m.p. 55°C. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2980, 2915, 2840, 2815 (CH), 1600, 1580, 1490 (C=C), 1215, 1045, 1020 (C−O). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 (m, 4 H, 9-, 9′-H_2), 1.57 (m, 4 H, 8-, 8′-H_2), 2.57 (t, *J* = 7.6 Hz, 4 H, 7-, 7′-H_2), 3.75, 3.76 (2 s, 12 H, $-OCH_3$), 6.66 (dd, *J* = 8.6, 3.0 Hz, 2 H, 4-, 4′-H), 6.72 (d, *J* = 3.0 Hz, 2 H, 6-, 6′-H), 6.75 (d, *J* = 8.6 Hz, 2 H, 3-, 3′-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.45 (C-9), 29.88 (C-8, -8′), 30.28 (C-7, -7′), 55.63, 56.94 ($-OCH_3$), 110.57 (C-4, -4′), 111.20 (C-3, -3′), 116.22 (C-6, -6′), 132.67 (C-1, -1′), 151.80 (C-2, -2′), 153.45 (C-5, -5′). − $C_{22}H_{30}O_4$ (358.5): calcd. C 73.71, H 8.44; found C 74.63, H 8.88.

1,6-Bis(2,5-dimethoxy-4-methylphenyl)hexane (**15b**): 2,5-Dimethoxytoluene (9.60 g, 62.5 mmol) was added at 0°C to a suspension of aluminium trichloride (9.30 g, 70.0 mmol) in dichloromethane (80 ml), then adipic acid dichloride (4.57 g, 25.0 mmol) in dichloromethane (20 ml). After stirring for 1 h at 0°C and 16 h at room temp., the mixture was poured into ice (150 g) and conc. H_2SO_4 (10 ml). Extraction with dichloromethane (3 × 200 ml), washing with saturated $NaHCO_3$ and removal of the solvent yielded a solid residue which was treated with acetone (100 ml) and 2 M sodium hydroxide (100 ml) for 20 min. After addition of further 2 M NaOH (100 ml) and heating to 100°C for 30 min, the product precipitated on cooling. The solid was washed with some cold ethanol and dried: **13b** (5.50 g, 56%) as colorless needles, m.p. 167°C. Hydrogenation of **13b** (5.85 g, 14.1 mmol) according to **15a** afforded crude **15b** (4.38 g). From methanol (100 ml) **15b** (3.99 g, 73%) as colorless needles, m.p. 87−88°C. − IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2920, 2840, 2815 (CH), 1500 (C=C), 1210, 1040 (C−O). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (mn, 4 H, 9-, 9′-H_2), 1.57 (m, 4 H, 8-, 8′-H_2), 2.20 (s, 3 H, $-CH_3$), 2.56 (t, *J* = 7.6 Hz, 4 H, 7-, 7′-H_2), 3.75, 3.77 (2 s, 12 H, $-OCH_3$), 6.63 (s, 2 H, 6-, 6′-H), 6.66 (s, 2 H, 3-, 3′-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.09 (q, $-CH_3$), 29.53 (t, C-9, -9′), 30.21 (t, C-8, -8′), 30.32 (t, C-7, -7′), 56.12, 56.17 (2 q, $-OCH_3$), 112.82 (d, C-6, -6′), 113.98 (d, C-3, -3′), 124.29 (s, C-4, -4′), 129.29 (s, C-1, -1′), 151.18, 151.52 (2 s, C-2, -2′, -5, -5′). − $C_{24}H_{34}O_4$ (386.4): calcd. C 74.61, H 8.87; found C 75.11, H 9.31.

1,6-Bis(4-bromo-2,5-dimethoxyphenyl)hexane (**15c**): Procedure see **6c**. Bromine (6.71 g, 42.0 mmol), **15a** (7.17 g, 20.0 mmol). Kugelrohr distillation (156°C, 0.01 Torr) of the crude product yielded **15c** (8.27 g, 80%) as a crystallizing oil, m.p. 85−86°C. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2940, 2920, 2885, 2830 (CH), 1490, 1480 (C=C), 1205, 1050, 1030 (C−O). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.36 (m, 4 H, 9-, 9′-H_2), 1.55 (m, 4 H, 8, -8′-H_2), 2.55 (t, *J* = 7.6 Hz, 4 H, 7-, 7′-H_2), 3.75, 3.83 (2 s, 12 H, $-OCH_3$), 6.72 (s, 2 H, 6-, 6′-H), 7.00 (s, 2 H, 3-, 3′-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ =

29.31 (t, C-9, -9′), 29.81 (t, C-8, -8′), 30.26 (t, C-7, -7′), 56.10, 56.98 (2 q, $-OCH_3$), 108.21 (s, C-4, -4′), 114.46 (d, C-6, -6′), 115.74 (d, C-3, -3′), 131.62 (s, C-1, -1′), 149.83 (s, C-2, -2′), 151.95 (s, C-5, -5′). − $C_{22}H_{38}Br_2O_4$ (516.3): calcd. C 51.18, H 5.47; found C 51.34, H 5.54.

α,ω-Bis(1,4-benzoquinon-2-yl)alkanes **16−20** *from α,ω-Bis(2,5-dimethoxyphenyl)alkanes* **2**, **6**, **9**, **14**, *and* **15**. − *General Procedure:* By adaptation of ref.[29] a solution of **16−20** in dichloromethane (DCM, 90−120 ml) was slowly added at 0°C under argon to boron tribromide (4.2 equiv.) in DCM (60−80 ml). After 16 h at room temp., the mixture was poured into ice and extracted with diethyl ether/acetone (3:1). The organic phase was washed with water (→ pH = 5) and dried (Na_2SO_4). After evaporation of the solvent, the residue was dissolved in diethyl ether/acetone/water (2:2:1, 150−200 ml) and a 2 M solution (4.2 equiv.) of chromium(IV) oxide in sulfuric acid (33%) was slowly added at 0°C. After stirring for 30 min, the mixture was extracted with DCM and the organic phase washed with water until the latter became colorless. Evaporation of the solvent yielded crude **21−25.**

1,2-Bis(1,4-benzoquinon-2-yl)ethane (**16a**): **2a** (4.54 g, 15.0 mmol) yielded crude **16a** (3.48 g, 96). From toluene/ethanol (1:1, 180 ml) yellow needles of **16a**, m.p. 198−199°C, dec. [ref.[8a]: 52%, m.p. 194°C (subl.); ref.[8b]: 67%, m.p. 185°C, dec.]. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (CH), 1645 (C=O), 1585 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 246 nm (4.51), 300 (3.43). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.67 (s, 4 H, $-CH_2-CH_2$), 6.59 (d, J = 2 Hz, 2 H, 3-H), 6.75 (dd, J = 10 Hz, 2 Hz, 2 H, 5-H), 6.79 (d, J = 10 Hz, 2 H, 6-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 27.71 ($-CH_2-CH_2-$), 133.08 (C-3), 136.51 (C-5)[a], 136.75 (C-6)[a], 147.46 (C-2), 187.06 (C-1)[b], 187.27 (C-4)[b]. − [a][b]Assignments interchangeable.

1,2-Bis(5-methyl-1,4-benzoquinon-2-yl)ethane (**16b**): **2b** (6.61 g, 20.0 mmol) afforded crude **16b** (4.67 g, 86%). From toluene/ethanol (1:1, 240 ml) yellow needles of **16b** (4.33 g, 80%), m.p. 198−199°C; (ref.[9]): 85%, m.p. 202−203°C (benzene). − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2980, 2960, 2920, 2900 (CH), 1650 (C=O), 1610 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 252 nm (4.57), 258 (4.51); sh[9]: 255.5 nm (4.54 in CH_2Cl_2). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.05 (d, J = 2 Hz, 6 H, $-CH_3$), 2.65 (s, 4 H, $-CH_2-CH_2-$), 6.55 (s, 2 H, 6-H), 6.62 (d, J = 2 Hz, 2 H, 3-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.50 (q, $-CH_3$), 27.44 (t, $-CH_2-CH_2$), 133.08 (d, C-3), 133.55 (d, C-6), 145.88 (s, C-5), 147.46 (s, C-2), 187.33 (s, C-1)[a], 187.81 (s, C-4)[a]. − [a]Assignments interchangeable.

1,2-Bis(5-bromo-1,4-benzoquinon-2-yl)ethane (**16c**): **2c** (6.90 g, 15.0 mmol) yielded crude **16c** (5.37 g, 90%). From toluene/ethanol (1:3, 360 ml) orange needles of **16c** (3.94 g, 60%), m.p. 212°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (CH), 1655, 1650 (C=O), 1585 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 267 nm (4.45). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.68 (s, 4 H, $-CH_2-CH_2$), 6.77 (s, 2 H, 3-H), 7.31 (s, 2 H, 6-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 27.68 ($-CH_2-CH_2$), 132.44 (C-3), 137.57 (C-5), 138.21 (C-6), 147.79 (C-2), 179.24 (C-4), 184.45 (C-1). − $C_{14}H_8Br_2O_4$ (400.0): calcd. C 42.04, H 2.02; found C 42.31, H 2.11.

1,3-Bis(1,4-benzoquinon-2-yl)propene (**17a**): **6a** (6.34 g, 20.0 mmol) afforded crude **17a** (4.70 g, 92%). From toluene/ethanol (1:4, 250 ml) yellow needles of **17a** (4.39 g, 86%), m.p. 148°C; ref.[11]: 41%, m.p. 149−150°C (subl.). − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2940 (CH), 1650 (C=O), 1590 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 247 nm (4.58), 318 (3.22); ref.[27]: 248 nm (4.62), 315 (3.22 in THF). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.76 (quint, J = 8 Hz, 2 H, $-CH_2-CH_2-CH_2-$), 2.50 (t, J = 8 Hz, 4 H, $-CH_2-CH_2-CH_2-$), 6.61 (d, J = 2 Hz, 2 H, 3-H), 6.74 (dd, J = 10, 2 Hz, 2 H, 5-H), 6.78 (d, J = 10 Hz, 2 H, 6-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 25.98 (t, $-CH_2-CH_2-CH_2-$), 28.71 (t, $-CH_2-CH_2-CH_2-$), 132.81 (d, C-3), 136.39 (d, C-5)[a], 136.75 (d, C-6)[a], 148.33 (s, C-2), 187.24 (s, C-1)[b], 187.48 (s, C-4)[b]. − [a][b]Assignments interchangeable.

1,3-Bis(5-methyl-1,4-benzoquinon-2-yl)propane (**17b**): **6b** (6.89 g, 20.0 mmol) yielded crude **17b** (4.79 g, 84%). From toluene/ethanol (1:4, 250 ml) yellow needles of **17b** (4.46 g, 78%), m.p. 176°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2940, 2920 (CH), 1645 (C=O), 1605 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 523 nm (4.48), 259 (4.43), sh. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.73 (quint, J = 7 Hz, 2 H, $-CH_2-CH_2-CH_2-$), 2.04 (d, J = 2 Hz, 6 H, $-CH_3$), 2.47 (t, J = 7 Hz, 4 H, $-CH_2-CH_2-CH_2$), 6.57 (s, 2 H, 3-H), 6.60 (d, J = 2 Hz, 2 H, 6-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.49 (q, $-CH_3$), 26.09 (t, $-CH_2-CH_2-CH_2-$), 28.45 (t, $-CH_2-CH_2-CH_2$), 132.83 (d, C-3), 133.56 (d, C-6), 145.75 (s, C-5), 148.36 (s, C-2), 187.54 (s, C-1)[a]. − [a]Assignments interchangeable. − $C_{17}H_{16}O_4$ (284.3): calcd. C 71.82, H 5.67; found C 71.66, H 5.71.

1,3-Bis(bromo-1,4-benzoquinon-2-yl)propane (**17c**): **6c** (8.48 g, 17.9 mmol) afforded crude **17c** (6.91 g, 93%). From toluene/ethanol (1:4, 250 ml) orange needles of **17c** (6.54 g, 88%), m.p. 148°C. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2940 (CH), 1665, 1665 (C=O), 1625, 1585 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 269 nm (4.48). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.76 (quint, J = 8 Hz, 2 H, $-CH_2-CH_2-CH_2-$), 2.51 (t, J = 8 Hz, 4 H, $-CH_2-CH_2-CH_2$), 6.79 (s, 2 H, 3-H), 7.28 (s, 2 H, 6-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.01 (t, $-CH_2-CH_2-CH_2-$), 132.14 (d, C-3), 137.41 (s, C-5), 138.20 (d, C-6), 148.75 (s, C-2), 179.38 (s, C-4), 184.60 (s, C-1). − $C_{15}H_{10}Nr_2O_4$ (414.0): calcd. C 43.51, H 2.43; found C 43.62, H 2.45.

1-(5-Methyl-1,4-benzoquinon-2-yl)-3-(1′,4′-benzoquinon-2′-yl)-propane (**17d**): **6d** (4.69 g, 15.0 mmol) yielded **17d** (3.12 g, 77%). From toluene/ethanol (1:4, 250 ml) soft orange needles of **17d** (2.81 g, 69%), m.p. 168°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2975, 2940, 2910(CH), 1650 (C=O), 1600, 1580 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 251 nm (4.51), 320 (2.99). − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.74 (quint, J = 7.7 Hz, 2 H, 8-H_2), 2.05 (d, J = 1.6 Hz, 3 H, $-CH_3$), 2.48, 2.49 (2 td, J = 7.7, 1.2 Hz, 4 H, 7-, 7′-H_2), 6.58 (t, J = 1.2 Hz, 1 H, 3-H), 6.61 (m, 2 H, 6-, 3′-H), 6.74 (dd, J = 10.1, 2.2 Hz, 1 H, 5′-H), 6.77 (d, J = 10.1 Hz, 1 H, 6′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.44 ($-CH_3$), 26.10 (C-8), 28.44 (C-7), 28.72 (C-7′), 132.82, 132.87 (C-3, -3′), 133.54 (C-6), 136.39, 136.78 (C-5′, -6′), 145.77 (C-5), 148.28, 148.43 (C-2, -2′), 187.24 (C-1′), 187.46 (C-1, -4′), 187.94 (C-4). − $C_{16}H_{14}O_4$ (270.3): calcd. C 71.10, H 5.22; found C 70.85, H 5.24.

1-(5-Bromo-1,4-benzoquinon-2-yl)-3-(5-methyl-1′,4′-benzoquinon-2′-yl)propane (**17e**): **6e** (4.09 g, 10.0 mmol) afforded **17e** (3.03 g, 87%). From toluene/ethanol (1:3, 1210 ml) tiny orange plates of **17e** (2.48 g, 81%), m.p. 150−151°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2935 (CH), 1655, 1640 (C=O), 1600, 1575 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 255 nm (sh, 4.46), 261 (4.47), 320 (sh, 2.86). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.75 (quint, J = 7.4 Hz, 2 H, 8-H_2), 2.05 (d, J = 1.5 Hz, 3 H, $-CH_3$), 2.47 (td, J = 7.4, 1.3 Hz, 2 H, 8′-H_2), 2.51 (td, J = 7.4, 1.3 Hz, 2 H, 8-H_2), 6.58 (t, J = 1.3 Hz, 1 H, 3′-H), 6.60 (q, J = 1.5 Hz, 1 H, 6′-H), 6.79 (t, J = 1.3 Hz, 1 H, 3-H), 7.28 (s, 1 H, 6-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.43 ($-CH_3$), 26.11 (C-8), 28.41 (C-7′), 28.60 (C-7), 132.09 (C-3), 132.93 (C-3′), 133.54 (C-6′), 137.40 (C-5), 138.25 (C-6), 145.82 (C-5′), 148.13 (C-2′), 149.07 (C-2), 179.42 (C-4), 184.60 (C-1), 187.45, 187.89 (C-1′, -4′). − $C_{16}H_{13}BrO_4$ (349.2): calcd. C 55.04, H 3.75, Br 22.88; found C 54.86, H 3.81, Br 22.74.

1,4-Bis(1,4-benzoquinon-2-yl)butane (**18a**): **9a** (61.61 g, 20.0 mmol) yielded **18a** (4.61 g, 85%). From toluene/ethanol (3:2, 250 ml) yellow microcrystals of **18a** (4.12 g, 76%), m.p. 179−180°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2940, 2920, 2880, 2860, 2810 (CH), 1645 (C=O), 1590 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 248 nm (4.54), 317 (3.18). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59 (tt, *J* = 6, 3 Hz, 4 H, 8, -8′-H$_2$), 2.46 (td, *J* = 6 Hz, 1.3 Hz, 4 H, 7-, 7′-H$_2$), 6.58 (dd, *J* = 2.0, 1.3 Hz, 2 H, 3, -3′-H), 6.74 (dd, *J* = 10.1, 2.0 Hz, 2 H, 5-, 5′-H); 6.77 (d, *J* = 10.1 Hz, 2 H, 6-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.61 (t, C-8, -8′), 28.78 (t, C-7, -7′), 132.67 (d, C-3, -3′), 136.33, 136.78 (2 d, C-5, -5′, -6, -6′), 148.91 (s, C-2, -2′), 187.36, 187.62 (C-1, -1′, -4, -4′). − $C_{16}H_{14}O_4$ (270.8): calcd. C 70.97, H 5.21; found C 70.80, H 5.29.

1,4-Bis(5-methyl-1,4-benzoquinon-2-yl)butane (**18b**): **9b** (4.48 g, 12.5 mmol) afforded **18b** (3.39 g, 91%). From toluene/ethanol (1:1, 180ml) small orange scales of **18b** (3.09 g, 83%), m.p. 186−187°C. − IR (KBr): $\tilde{\nu}$ = 3035 cm^{-1}, 2980, 2940, 2920, 2880, 2860 (CH), 1635 (C=O), 1600 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 253 nm (4.59), 259 (sh, 4.54), 315 (2.88). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55 (m, 4 H, 8-, 8′-H$_2$), 2.03 (d, *J* = 1.6 Hz, 6 H, $-CH_3$), 2.42 (m, 7-, 7′-H$_2$), 6.53 (t, *J* = 1.4 Hz, 2 H, 3-, 3′-H), 6.58 (q, *J* = 1.6 Hz, 2 H, 6-, 6′-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.46 (q, $-CH_3$), 27.65 (t, C-8, -8′), 28.49 (t, C-7, -7′), 132.66 (d, C-3, -3′), 133.54 (d, C-6, -6′), 145.65 (s, C-5, -5′), 148.91 (s, C-2, -2′), 187.36, 187.62 (C-1, -1′, -4, -4′). − $C_{18}H_{18}O_4$ (298.1) calcd. C 72.47, H 6.08; found C 72.40, H 5.99.

1,4-Bis(5-bromo-1,4-benzoquinon-2-yl)butane (**18c**): **9c** (6.10 g, 12.5 mmol) yielded **18c** (4.33 g, 81%). From chlorobenzene (200 ml) tiny orange needles of **18c** (4.39 g, 81%), m.p. 202−203°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2940, 2895, 2880, 2860 (CH), 1640 (C=O), 1575 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 268 nm (4.45), 337 (2.99). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.67 (C-8, -8′), 28.71 (C-7, -7′), 132.05 (C-3, -3′), 137.43 (C-5, -5′), 138.30 (C-6, -6′), 149.45 (s, C-2, -2′), 179.54 (C-4, -4′), 184.72 (C-1, -1′). − $C_{16}H_{12}Br_2O_4$ (428.1): calcd. C 44.89, H 2.83, Br 37.33; found C 44.93, H 2.88, Br 37.15.

1,5-Bis(1,4-benzoquinon-2-yl)pentane (**19a**): **14a** (8.66 g, 25.0 mmol) yielded **19a** (6.31 g, 89%). After flash chromatography (DMC) orange needles of **19a** (4.60 g, 65%); ref.[24]: 70%, m.p. 84.5−85.5°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2940, 2920, 2890, 2850 (CH), 1650 (C=O), 1590 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 2.48 nm (4.54). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.53 (m, 6 H, 8-, 9-H$_2$), 2.44 (t, *J* = 6.8 Hz, 4 H, 7-, 7′-H$_2$), 6.58 (d, *J* = 2 Hz, 2 H, 3-, 3′-H), 6.73 (dd, *J* = 10, 2 Hz, 5-, 5′-H), 6.77 (d, *J* = 10 Hz, 2 H, 6-, 6′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.53 (C-9), 28.87 (C-7, -7′, -8, -8′), 132.47 (C-3, -3′), 136.27, 136.75 (C-5, -5′, -6, -6′), 149.25 (C-2, -2′), 187.39, 187.66 (C-1, -1′, -4, -4′).

1,5-Bis(5-methyl-1,4-benzoquinon-2-yl)pentane (**19b**): **14b** (9.31 g, 25.0 mmol) afforded **19b** (7.30 g, 93%). From ethanol (150 ml) yellow needles of **19b** (6.82 g, 87%), m.p. 119°C. − IR (KBr): $\tilde{\nu}$ = 3035 cm^{-1}, 2940, 2915, 2870, 2855 (CH), 1645 (C=O), 1600 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 253 nm (4.60), 260 (sh, 4.55). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.50 (m, 6 H, 8-, 8′-, 9-H$_2$), 2.04 (d, *J* = 1.6 Hz, 6 H, $-CH_3$), 2.41 (td, *J* = 6.8, 1.4 Hz, 4 H, 7-, 7′-H$_2$=, 6.54 (t, *J* = 1.4 Hz, 2 H, 3-, 3′-H), 6.59 (q, *J* = 1.6 Hz, 2 H, 6-, 6′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.32 ($-CH_3$), 27.58 (C-9), 28.54, 28.87 (C-7, -7′, -8, -8′), 132.48 (C-3, -3′), 133.51 (C-6, -6′), 145.52 (C-5, -5′), 149.19 (C-2, -2′), 187.61, 188.03 (C-1, -1′, -4, -4′). − $C_{19}H_{20}O_4$ (312.4): calcd. C 73.06, H 6.45; found C 73.46, H 6.39.

1,5-Bis(5-bromo-1,4-benzoquinon-2-yl)pentane (**19c**): **14c** (10.0 g, 20.0 mmol) afforded **19c** (8.30 g, 94%). From ethanol (200 ml) small orange scales of **19c** (7.31 g, 83%), m.p. 119°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2855 (CH), 1650 (C=O), 1585 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 268 nm (4.48). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.52 (m, 6 H, 8-, 8′-, 9-H$_2$), 2.45 (t, *J* = 6.9 Hz, 4 H, 7-, 7′-H$_2$), 6.76 (t, *J* = 1.3 Hz, 2 H, 3′-H), 7.29 (s, 2 H, 6-, 6′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.49 (C-9), 28.75, 28.84 (C-7, -7′, -8, -8′), 131.78 (C-3, -3′), 137.24 (C-5, -5′), 138.21 (C-6, -6′), 149.80 (C-2, -2′), 179.51 (C-4, -4′), 184.75 (C-1, -1′). − $C_{17}H_{14}Br_2O_4$ (442.1): calcd. C 46.19, H 3.19; found C 46.57, H 3.19.

1,6-Bis(1,4-benzoquinon-2-yl)hexane (**20a**): **15a** (5.37 g, 15.0 mmol) afforded **20a** (3.81 g, 85%). From toluene/ethanol (1:2, 180 ml) yellow microcrystalline powder of **20a** (3.68 g, 82%), m.p. 154°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2890, 2840 (CH), 1650 (C=O), 1590 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 248 nm (4.56), 318 (3.22). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (m, 4 H, 9-, 9′-H$_2$), 1.52 (m, 4 H, 8-, 8′-H$_2$), 2.42 (td, *J* = 7.5, 1.3 Hz, 4 H, 7-, 7′-H$_2$), 6.57 (dt, *J* = 2.1, 1.3 Hz, 2 H, 3-, 3′-H), 6.72 (dd, *J* = 10.0, 2.1 Hz, 2 H, 5-, 5′-H), 6.77 (d, *J* = 10.0 Hz, 2 H, 6-, 6′-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.70 (t, C-9, -9′), 28.99 (t, C-7, -7′, -8, -8′), 132.47 (d, C-3, -3′), 136.30, 136.82 (2 d, C-5, -5′, -6,-6′); 149.49 (s, C-2, -2′), 187.50, 187.79 (2 s, C-1, -1′, -4, -4′). − $C_{18}H_{14}O_4$ (298.3): calcd. C 72.47, H 6.08; found C 72.73, H 6.14.

1,5-Bis(5-methyl-1,4-benzoquinon-2-yl)hexane (**20b**): **15b** (5.80 g, 15.0 mmol) yielded **20b** (4.40 g, 89%). From toluene/ethanol (2:1, 300ml) small yellow scales of **20b** (4.26 g, 87%), m.p. 168°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2965, 2910, 2880, 2825 (CH), 1635 (C=O), 1600 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 254 nm (4.57), 261 (sh, 4.53), 326 (2.99). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (m, 4 H, 9-, 9′-H$_2$), 1.50 (m, 4 H, 8-, -8′-H$_2$), 2.04 (d, *J* = 1.5 Hz, 6 H, $-CH_3$), 2.40 (td, *J* = 7.4,1.2 Hz, 4 H, 7, -7′-H$_2$), 6.54 (t, *J* = 1.2 Hz, 2 H, 3-, 3′-H), 6.59 (q, *J* = 1.5 Hz, 2 H, 6-, 6′-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.56 (q, $-CH_3$), 27.74 (t, C-9, -9′), 28.69, 28.99 (2 t, C-7, -7′, -8, -8′), 132.48 (d, C-3, -3′), 133.58 (d, C-6, -6′), 145.57 (s, C-5, -5′), 149.42 (s,C-2, -2′), 187.80, 188.25 (2 s, C-1,-1′, -4, -4′). − $C_{20}H_{22}O_4$ (326.4): calcd. C 73.60, H 6.79; found C 73.43, H 6.90.

1,6-Bis(5-bromo-1,4-benzoquinon-2-yl)hexane (**20c**): **15c** (7.74 g, 15.0 mmol) afforded **20c** (5.74 g, 84%). From toluene (200 ml) small orange needles of **20c** (5.69 g, 83%), m.p. 183°C. − IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 2925, 2835 (CH), 1640 (C=O), 1575 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 270 nm (4.44), 3.36 (2.97). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40 (m, 4 H, 9-, 9′-H$_2$), 1.51 (m, 4 H, 8-, 8′-H$_2$), 2.43 (td, *J* = 8.0, 1.2 Hz, 4 H, 7-, 7′-H$_2$), 6.74 (t, *J* = 1.2 Hz, 2 H, 3-, 3′-H), 7.27 (s, 2 H, 6-, 6′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.69, C-9, -9′), 28.90 (C-7, -7′, -8, -8′), 131.78 (C-3, -3′), 137.32 (C-5, -5′), 138.30 (C-6, -6′), 150.05 (C-2, -2′), 179.65 (C-4, -4′), 184.88 (C-1, -1′). − $C_{18}H_{16}Br_2O_4$ (456.1): calcd. C 47.40, H 3.54; found C 47.60, H 3.49.

a,ω-Bis[1,4-bis(cyanimino)benzoquinon-2-yl]alkanes **22−25** *from Bis(quinones)* **17−20**. − *General Procedure:* Bis(trimethylsilyl)carbodiimide (SCI, 80 mmol) was added at 0°C to titanium tetrachloride (100ml) in dry DCM (50 ml) under argon. Then, bis-(quinones) **17−20** (5 mmol) in DCM (50−200 ml, according to their solubility) were slowly added. After stirring for 26−48 h at room temperature, the mixture was poured on ice. − Version A (VA): Extraction (3−5 ×) with DCM, washing of the organic phase (→ pH = 5), concentration to 20−30 ml, addition of PE and cooling in the refrigirator. The precipitate was isolated and washed with PE. − Version B (VB): The precipitate was isolated, washed with water and some cold ethanol, then dried. − In both cases the

Table 5. Physical data of CT complexes from bis(DCNQIs) and TTF

Compound	Yield (%)	M.p. [°C]	IR (KBr) $\tilde{\nu}$ [−1]	Formula	Mol. mass	C C	H H	N[a] N[b]
(**22a**)TTF$_2$	25		2100 br.	$C_{31}H_{20}N_8S_8$	761.1	48.92 48.13	2.65 2.83	14.72 13.71
(**23a**)TTF$_{2.8}$	66	92	2800 br.	$C_{37}H_{25}N_8S_{11}$	934.3	47.09 46.71	2.71 2.92	11.94 12.15
(**24a**)TTF$_{2.5}$	71	104	2090	$C_{36}H_{26}N_8S_{10}$	891.3	48.51 48.22	2.94 2.69	12.57 12.70
(**25a**)TTF$_{1.9}$	66	124	2140	$C_{33}H_{26}N_8S_8$	782.7	51.25 51.69	3.30 3.39	14.32 14.15
(**22c**)TTF$_2$	90	135	2100 br.	$C_{31}H_{18}Br_2N_8S_8$	918.9	40.52 40.94	1.97 2.00	12.19 12.13
(**23c**)TTF$_{2.0}$	89	114	2090	$C_{32}H_{20}Br_2N_8S_8$	932.9	41.20 40.87	2.16 2.13	12.01 12.34
(**24c**)TTF$_{2.2}$	79	108	2090	$C_{34}H_{25}N_8S_9$	891.3	41.58 41.05	2.33 2.76	11.34 11.42
(**25c**)TTF$_{2.0}$	70	84	2100 br.	$C_{34}H_{24}Br_2N_8S_8$	960.9	42.49 42.68	2.52 2.82	11.66 13.44

[a] C, H, N calculated. − [b] C, H, N found.

hardly soluble crude products were purified by hot continous extraction (CE) and only in a few cases by recrystallization. Due to very low solubilities, NMR spectra could not be recorded.

1,3-Bis[1,4-bis(cyanimino)benzoquinon-2-yl]propane (**22a**): **17a**, by VA crude **22a** (0.40 g, 23%) was isolated. Recrystallization of 280 mg from chlorobenzene (90 ml) yielded **22a** (167 mg, 10%) as an amorphous olive-colored powder, dec. 150°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2930 (CH), 2165 (C≡N), 1575 (C=C), 1545 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 333 nm (4.72). − $C_{19}H_{12}N_8$ (352.4): calcd. C 64.76, H 3.43, N 31.80; found C 63.96, H 3.39, N 30.89.

1,3-Bis[1,4-bis(cyanimino)-5-methylbenzoquinon-2-yl]propane (**22b**): **17b,** by VB crude **22b** (1.83 g) was isolated. CE with DCM (50 ml, 8 d) microcrystalline orange-brown powder of **22b** (0.96 g, 50%), dec. 192°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3020, 2990, 2980, 2940 (CH), 2170 (C≡N), 15.85 (C=C), 1535 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 342 nm (4.77). − $C_{21}H_{16}N_8$ (380.4): calcd. C 66.31, H 4.24, N 29.46; found C 66.14, H 4.25, N 29.05.

1,3-Bis[5-bromo-1,4-bis(cyanimino)benzoquinon-2-yl]propane (**22c**): **17c**, VA afforded **22c** (2.36 g). CE with DCM (50 ml, 4 d), cooling to −30°C yielded amorphous ochre-colored **22c** (1.13 g, 44%), dec. 184°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920 (CH), 2165 (C≡N), 1555 (C=C), 1540 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 349 nm (4.71), 362 (4.65) sh. − $C_{19}H_{10}Br_2N_8$ (510.2): calcd. C 44.73, H 1.98, N 21.96; found C 44.43, H 1.82, N 21.97.

1-[1,4-Bis(cyanimino)-5-methylbenzoquinon-2-yl]-3-[1′,4′-bis-(cyanimino)benzoquinon-2′-yl]propane (**22d**): **17d**, VA afforded **22d** (1.34 g). CE with DCM/PE (55−56°C, 1:1, 4 d) yielded **22d** (0.45 g, 24%) as yellow-greenish amorphous powder, dec. 185°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (CH), 2160 (C≡N), 1575, 1565 (C=C), 1530 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 333 nm (4.63), 360 (sh, 4.45). − $C_{20}H_{14}N_8$ (366.4): calcd. C 65.56, H 3.84, N 30.58; found C 66.28, H 3.63, N 30.37.

1-[5-Bromo-1,4-bis(cyanimino)benzoquinon-2-yl]-3-[1′,4′-bis-(cyanimino)-5′-methylbenzoquinon-2′-yl]propane (**22e**): **17e**, VB yielded crude **22e** (1.18 g). EC with DCM (75 ml) yielded **22e** (6.46 g, 21%) as an ochre-colored amorphous powder, dec. 174°C. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (CH), 2170 (C≡N), 1580 (C=C), 1535 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 343 nm (4.63), 361 (sh, 4.48). − $C_{20}H_{13}BrN_6$ (445.3): calcd. C 53.95, H 2.94, N 25.17; found C 53.96, H 2.95, N 25.42.

1,4-Bis[1,4-bis(cyanimino)benzoquinon-2-yl]butane (**23a**): **18a**, VA yielded a crude product (0.60 g). CE with DCM/PE (55−65°C, 2:1, 45 ml, 4 d) brownish green amorphous powder of **23a** (0.46 g, 25%), dec. 140°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2930, 2850 (CH), 2170 (C≡N), 1560 (C=C), 1545 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 333 nm (4.67), 343 (sh, 464). − $C_{20}H_{14}N_8$ (366.4): calcd. C 65.56, H 3.85, N 30.58; found C 65.27, H 3.68, N 30.20.

1,4-Bis[1,4-bis(cyanimino)-5-methylbenzoquinon-2-yl]butane (**23b**): **18b**, VB yielded a yellow powder (1.14 g). CE with DCM (75 ml, 4 d) afforded **23b** as a yellow greenish powder (0.77 g, 39%), dec. 164°C. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2950, 2920, 2855 (CH), 2165 (C≡N), 1575 (C=C), 1535 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 340 nm (4.61), 361 (sh, 4.43). − $C_{22}H_{18}N_8$ (394.4): calcd. C 66.99, H 4.60, N 28.41; found C 66.75, H 4.68, N 28.16.

1,4-Bis[5-bromo-1,4-bis(cyanimino)benzoquinon-2-yl]butane (**23c**): **18c**, VB afforded an orange powder (1.18 g). CE with DCM (90 ml, 3 d) yielded an orange powder of **23c** (0.48 g, 37%). − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2955, 2925, 2860 (CH), 2170 (C≡N), 1550 (C=C), 1540 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 347 nm (4.53), 363 (sh, 4.38). − $C_{20}H_{12}Br_2N_8$ (524.2): calcd. C 45.83, H 2.31, N 21.38; found C 45.85, H 2.34, N 21.54.

1,5-Bis[1,4-bis(cyanimino)benzoquinon-2-yl]pentane (**24a**): **19a**, by VA an ochre-colored product (0.91 g) was isolated. CE with DCM/PE (1:1, 4 d) yielded a yellow powder of **24a** (0.55 g, 27%), dec. 130°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2850 (CH), 2160 (C≡N), 1570 (C=C), 1545 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 333 nm (4.74), 343 (sh, 4.72). − $C_{21}H_{16}N_8$ (380.4): calcd. C 66.30, H 4.24, N 29.46; found C 66.53, H 4.18, N 29.67.

1,5-Bis[1,4-bis(cyanimino)-5-methylbenzoquinon-2-yl]pentane (**24b**): **19b**, by VAP an olive-colored product (1.67 g) was obtained. CE with DCM (75 ml, 4 d) yielded an olive-colored amorphous product (1.37 g, 67%), dec. 162°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2930, 2850 (CH), 2160 (C≡N), 1570 (C=C), 1535 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 343 nm (4.77), 360 (sh, 4.63). − $C_{23}H_{20}N_8$ (408.5): calcd. C 67.63, H 4.94, N 27.43; found C 67.54, H 4.87, N 27.36.

1,5-Bis[5-bromo-1,4-bis(cyanimino)benzoquinon-2-yl]pentane (**24c**): **19c**, by VA a khaki-colored product (1.87 g) was obtained. CE with DCM (40 ml, 3 d) yielded an amorphous ochre-colored powder of **24c** (1.51 g, 57%), dec. 159°C. − IR (KBr): $\tilde{\nu}$ = 3040

Table 6. Physical data of bis(DCNQI) copper salts

Compound	Yield (%)	M.p. [°C]	IR (KBr) $\tilde{\nu}$ [$^{-1}$]	Formula	Mol. mass	C	H	Cu	N[a]
						C	H	Cu	N[b]
(**22a**)Cu_2	84	81	2120 br.	$C_{19}H_{12}Cu_2N_8$	479.5	47.59	2.52		23.37
						47.72	2.67		23.34
(**23a**)$Cu_{1.8}I_{2(0.8)}$	93	93	2130			45.19	2.65	21.52	21.08
						45.34	3.01	21.14	20.33
(**24a**)$Cu_{1.6}I_{2(0.2)}$	83	101	2130	$C_{21}H_{16}Cu_{1.6}I_{2(0.2)}N_8$	532.9	47.34	3.03	19.08	21.03
						47.43	3.09	19.53	20.73
(**25a**)$Cu_{1.8}I_{2(0.2)}$	76	87	2120 br.	$C_{22}H_{18}Cu_{1.8}I_{2(0.2)}N_8$	559.6	47.22	3.24	20.44	20.02
						46.75	3.30	20.48	19.27
(**22b**)$Cu_{1.9}$	61	78	2130 br.	$C_{21}H_{16}Cu_{1.9}N_8$	505.2	50.60	3.24	−	22.48
						50.52	3.37	−	22.33
(**23b**)Cu_2	53	124	2100 br.	$C_{20}H_{14}Cu_2N_8$	520.0	50.67	3.48	24.37	21.49
						50.84	3.78	25.13	21.52
(**24b**)$Cu_{1.8}I_{2(0.6)}$	95	130	2110	$C_{23}H_{20}Cu_{1.8}I_{2(0.6)}N_8$	681.5	40.91	2.99	16.94	16.60
						40.90	2.73	17.59	17.07
(**22d**)$Cu_{1.7}I_{2(0.3)}$	76	78	2110 br.	$C_{21}H_{16}Cu_{1.6}I_{2(0.3)}N_2$	549.6	44.67	2.85	19.13	19.85
						45.29	2.81	19.48	19.82
(**22e**)$Cu_{1.3}I_{2(0.3)}$	92	75	2120 br.	$C_{20}H_{13}BrCu_{1.3}I_{2(0.3)}N_8$	629.5	38.16	2.08	17.16	17.80
						38.99	2.43	16.65	17.42
(**22c**)$Cu_{1.8}$	88	80	2160	$C_{19}H_{10}Br_2N_8$	627.9	36.72	1.62	−	18.03
						36.54	1.87	−	17.96
(**23c**)$Cu_{1.0}I_{2(0.5)}$	49	114	2110 br.	$C_{20}H_{12}Br_2CuI_{2(0.5)}N_8$	638.5	37.62	1.89	10.00	17.55
						37.09	2.09	9.81	17.24
(**24c**)$Cu_{1.8}I_{2(0.2)}$	84	100	2140	$C_{21}H_{14}Br_2Cu_{1.8}I_{2(0.2)}N_8$	703.4	35.86	2.01	16.26	15.92
						35.73	2.42	16.10	15.52
(**25c**)$Cu_{1.6}I_{2(0.1)}$	88	80	2140 br.	$C_{22}H_{16}Br_2Cu_{1.6}I_{2(0.1)}N_8$	679.3	38.90	2.37	14.97	16.50
						39.11	2.35	14.59	15.95

[a] C, H, Cu, N, calculated. − [b] C, H, Cu, N found.

cm^{-1}, 2950, 2925, 2860 (CH), 2180 (C≡N), 1565 (C=C), 1550 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 348 nm (4.76), 363 (sh, 4.64). − $C_{21}H_{14}Br_2N_8$ (538.2): calcd. C 46.86, H 2.62, N 20.82; found C 47.04, H 2.60, N 20.73.

1,6-Bis[1,4-bis(cyanimino)benzoquinon-2-yl]hexane (**25a**): **20a**, VA yielded a brownish powder (0.61 g). From CE with DCM/PE (1:1, 40 ml, 3 d) a yellow amorphous powder of **25a** (0.35 g, 18%) was obtained, dec. 136°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2930, 2850 (CH), 2170 (C≡N), 1570 (C=C), 1540 (C=O). − UV (CH_3CN): λ_{max} (lg ε) = 333 nm (4.67), 342 (sh, 4.65). − $C_{22}H_{18}N_8$ (395.4): calcd. C 66.99, H 4.60, N 28.41; found C 65.91, H 4.60, N 27.90.

1,6-Bis[1,4-bis(cyanimino)-5-methylbenzoquinone-2-yl]hexane (**25b**): **20b**, VB yielded an olive-colored powder (1.18 g). From CE with DCM/PE (1:1, 80 ml, 3 d) a yellow amorphous powder of **25b** (0.61 g, 29%) was isolated, dec. 182°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2920, 2830 (CH), 2160 (C≡N), 1575 (C=C), 1530 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 343 nm (4.71), 360 (sh, 4.53). − $C_{24}H_{22}N_8$ (422.5): calcd. C 68.23, H 5.25, N 26.52; found C 68.02, H 5.56, N 25.97.

1,6-Bis[5-bromo-1,4-bis(cyanimino)benzoquinon-2-yl]hexane (**25c**): **20c**, VB afforded a brown powder (1.45 g). CE with DCM/PE (2:1, 90 ml, 3 d) yielded a yellow greenish amorphous powder of **25c** (0.99 g, 36%), dec. 170°C. − IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 2925, 2850 (CH), 2170 (C≡N), 1655 (C=C), 1640 (C=N). − UV (CH_3CN): λ_{max} (lg ε) = 348 nm (4.71), 363 (4.59). − $C_{22}H_{16}Br_2N_8$ (552.2): calcd. C 47.85, H 2.92, N 20.29; found C 46.96, H 2.98, N 19.79.

General Procedure for CT Complexes from DCNQIs **21**−**25** *and TTF:* DCNQIs **21**−**25** (100 μmol) were dissolved in hot acetonitrile (AN) (15−25 ml) or in a mixture with dichloromethane (+ 15−20 ml). After rapid cooling, a degassed solution of TTF (200 μmol) in AN was added. On stirring (15−30 min) a dark precipitate was formed in the dark green solution. After cooling (−30°C, 12 h), the precipitate was separated, washed with AN and PE (1 ml each) and dried over silica gel. The products were black to dark violet (microcrystalline) powders.

General Procedure for Radical Anion Salts from DCNQIs **21**−**25** *and Copper(I) Iodide:* DCNQIs **21**−**25** (100 μmol) were dissolved as in the preceding procedure. To this solution copper(I) iodide (500 μmol) in 5 ml of AN was added and the mixture refluxed (15 min). On cooling a dark precipitate was formed from the dark green solution. After further cooling (−30°C, 12 h), the product was isolated, washed with AN and PE (1 ml each) and dried over silica gel.

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