Synthesis and Linear Optical Properties of Tris(catecholato)metal(III,IV) Complexes with Acceptor-Substituted Ligands

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Dedicated to the memory of Prof. Dr. Rüdiger Wortmann (1959–2005)

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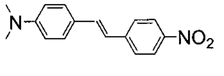
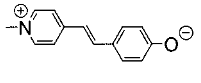
The synthesis of C_3-symmetric chromophores (**2–4**, **9**, **10**, **14**) with acceptor-substituted catecholato ligands and different central metal atoms (Si, Al, Ti) is described. These complexes might serve as octupolar chromophores with first-order nonlinear optical properties. UV/Vis spectroscopic investigations show a red-shift of the lowest-energy charge-transfer band on going from $\mathrm{Si^{IV}}$, $\mathrm{Al^{III}}$ to $\mathrm{Ti^{IV}}$ complexes, dependent on the increasing ionic character of the M–O bond.

Introduction

Over the past two decades, there has been considerable interest in the nonlinear optical (NLO) properties of organic and organometallic materials because of their potential application in various fields such as telecommunications, optical data storage and optical information processing. Many organic chromophores possess very high NLO efficiencies which derive from the high polarisability of electrons in unsaturated systems.[1–6] In one-dimensional NLO chromophores, in which a π-system is terminated by an electron acceptor and a donor, the electronic structure can be described by a mixture of a neutral valence-bond structure and a polar charge-separated mesomeric structure. The dipole moments of the ground and the first excited charge-transfer (CT) state depend on the degree of mixing. Those species, in which the neutral mesomeric structure constitutes the major part of the ground-state wave function, have a small ground-state dipole moment but a high dipole moment in the excited state. The prototype is 4-(dimethylamino)-4′-nitrostilbene (DANS).[3,4] Those systems, in which the dipolar mesomeric structure is the one which dominates the ground state, display zwitterionic character in the ground state but have a small dipole moment in the excited state. Brooker's dye is the prototype.[7,8]



DANS



Brooker´s dye

While most NLO chromophores are one-dimensional and show, owing to the difference of the ground- and excited-state dipole moments, a strong solvatochromism, there are also D_3-symmetrical two-dimensional "octupolar" NLO chromophores which have the advantage that they do not show solvatochromism and, therefore, no loss of transparency in a polar environment. This is a consequence of the vanishing dipole moments in a D_3-symmetric chromophore.[9–11] Therefore, in recent years many investigations were devoted to this type of NLO chromophore.[2,12–16]

Although Brooker's dye shows exceptionally high quadratic NLO properties, its accurate investigation is hampered because of the sensitivity of the electronic structure to protonation or even because of hydrogen bonding of the phenolate oxygen atom.[17–23] Therefore, the goal of this investigation is to synthesise octupolar chromophores in which the phenolate part of a chromophore ligand is complexed by a metal ion in order to reduce its sensitivity to protic impurities. On the other hand, the metal ion serves as a template to organise three chromophores in a threefold symmetric arrangement. In order to gain thermodynamic stability, we used ligands based on catecholate rather than on phenolate as in Brooker's dye. The metal ions are $\mathrm{Al^{III}}$,[24] $\mathrm{Ti^{IV}}$,[25–27] and $\mathrm{Si^{IV}}$[28,29] because these ions are known to form stable complexes with catecholate. The ions also form highly polar bonds to oxygen atoms, which will allow the catecholate to retain most of its anionic electronic structure, which is important in order to serve as a good electron donor in the ligand chromophores. The ligands used are given below. While **1** is derived from caffeic acid that has a carboxylic ester function as the electron acceptor, the ligands **8** and **13** have a nitro and a trimethylammonio group, respectively, as the acceptor functionalities. In the

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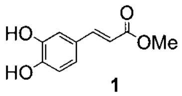
forthcoming sections we describe the syntheses and the linear optical properties of some metal complexes derived from the above-mentioned ligands.



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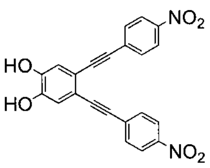

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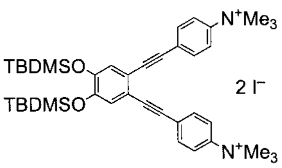

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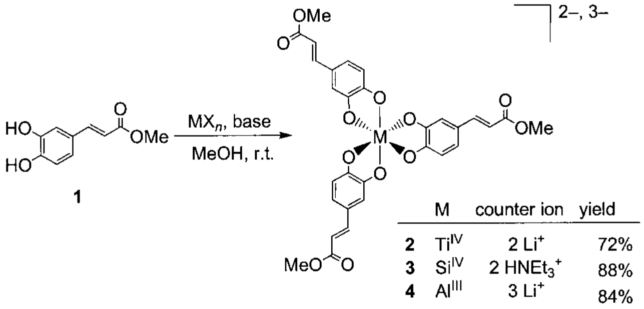
Results and Discussion

Synthesis and Characterisation

The synthesis of the (catecholato)M (M = metal) complexes **2**–**4** is illustrated in Scheme 1. The tris(catecholato)-Ti^{IV} complex **2** has been prepared in high yield using a procedure by Albrecht et al.[25,30]



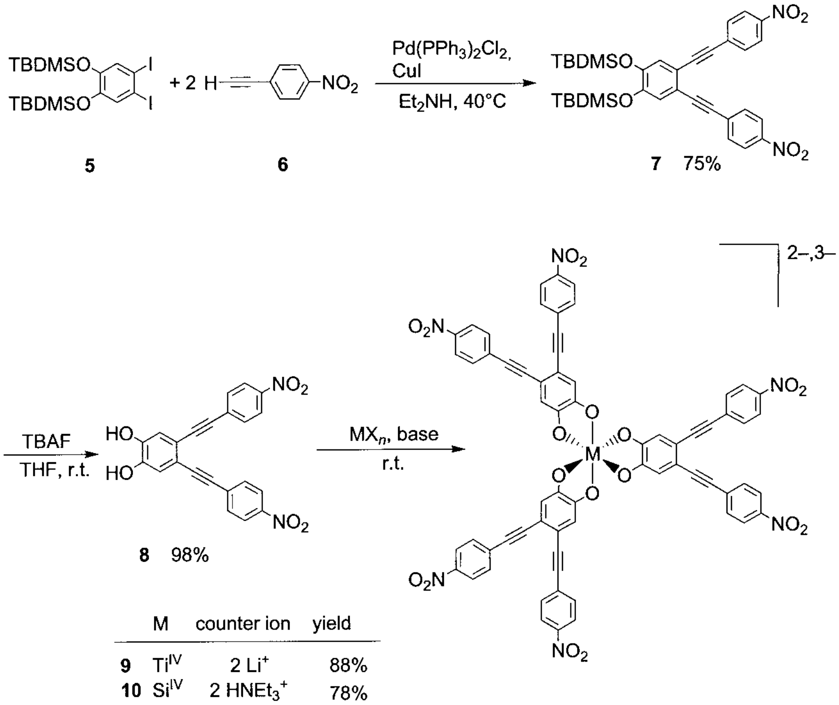
	M	counter ion	yield
2	Ti^{IV}	2 Li$^+$	72%
3	Si^{IV}	2 HNEt$_3^+$	88%
4	Al^{III}	3 Li$^+$	84%

Scheme 1. Synthesis of octupolar (catecholato)M^{IV,III} complexes **2**–**4**.

To explore the preparation of tris(catecholato) complexes with different central atoms, **1** was used as an easily accessible ligand. In case of the Ti^{IV} and Al^{III} complexes Li_2CO_3 was used as the base. For the Si^{IV} complex **3** triethylamine was used as the base for the preparation. NMR and IR spectroscopic investigations confirm the formation of the complexes. An intense band occurs in the IR spectra at about 1200–1300 cm^{-1} which is typical of C–O stretching modes in catecholato–metal structures.[24,31] In the case of the unsymmetrical ligand **1** diastereomeric complexes form which we were unable to separate. These diastereomers are likely to show slightly different optical properties, which are not considered in the following text.

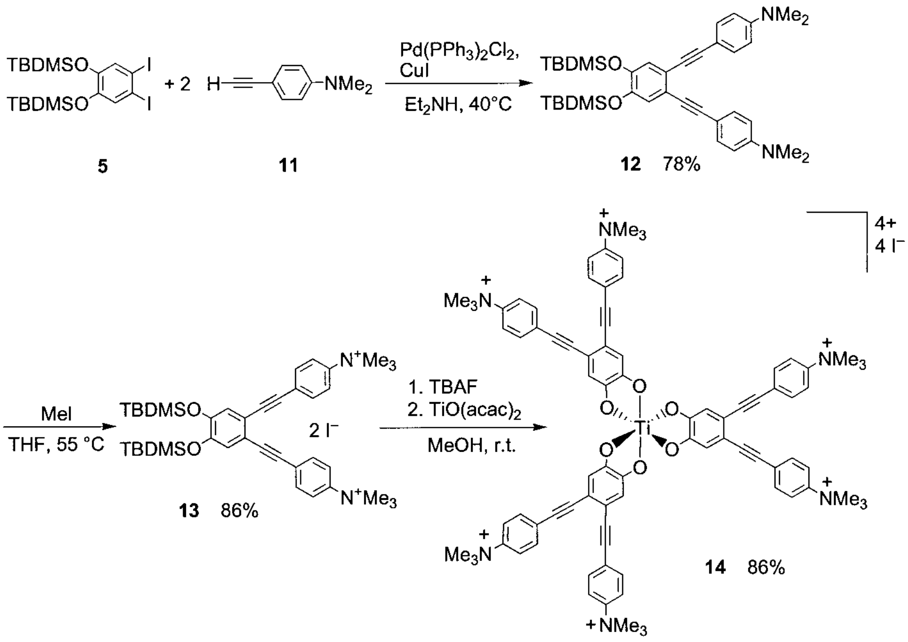
In order to avoid problems with diastomeric mixtures, 4,5-substituted catecholate systems were used to synthesise D_3-symmetrical complexes that will only consist of enantiomers.

The ligands **8** and **13** were prepared starting from the *tert*-butyldimethylsilyl-(TBDMS-)protected diiodo compound **5** which was synthesised according to Lulinski et al. and Kinder et al.[31,32] Using Hagihara coupling reaction conditions, compound **5** and 2 equiv. of **6** gave the 4,5-disubstituted ligand **7** in 75% yield. The reaction time has to be limited to 2 h because of the increasing formation of by-products with a prolonged reaction time. Deprotection of the TBDMS group led to the catechol ligand **8** in high yields (Scheme 2). The Ti^{IV} (**9**) and Si^{IV} complexes (**10**) were prepared in the same way as the caffeic acid complexes. Although the corresponding Al^{III} complex could be synthesised in an analogous manner, we were unable to purify this complex.



	M	counter ion	yield
9	Ti^{IV}	2 Li$^+$	88%
10	Si^{IV}	2 HNEt$_3^+$	78%

Scheme 2. Syntheses of the acceptor-substituted catechol ligand **8** and the corresponding octupolar Ti^{IV} (**9**) and Si^{IV} complexes (**10**).



Scheme 3. Syntheses of the TBDMS-protected acceptor-substituted catechol ligand **13** and the corresponding octupolar Ti^{IV} complex **14**.

Ligand **13** was built up in the same way as alkyne **8**: the alkyne **11** was coupled with **5** in a palladium-catalysed reaction to give compound **12**. Subsequently, the amino groups of **12** were quaternised with methyl iodide. The Ti^{IV} complex **14** was prepared by in situ deprotection of **13** and reaction with TiO(acac)$_2$ (Scheme 3).

UV/Vis Absorption Spectra

Owing to the ionic character of all complexes, absorption spectra could only be recorded in relatively polar solvents. The UV/Vis spectra of the free ligand **1** show a concentration-dependent behaviour in DMSO. At high concentrations **1** has an absorption maximum at λ_{max} = 335 nm. Dilution leads to the formation of a new band at 425 nm, associated with an increase of this band (Figure 1).

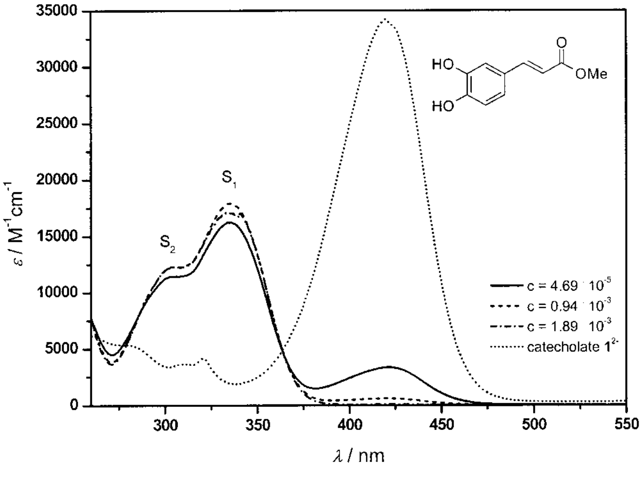


Figure 1. Concentration-dependent UV/Vis spectra of **1** and the catecholate **1**$^{2-}$ in DMSO.

The reason for this behaviour is, as for ligand **8**, the concentration-dependent shift of the acid/base equilibrium to the deprotonated species and finally to the catecholate dianion **1**$^{2-}$. Quantitative preparation of the catecholate dianion **1**$^{2-}$ by adding sodium *tert*-butoxide to a solution of **1** results in a bathochromic shift and in the formation of an intense band at λ_{max} = 420 nm which corresponds to the one observed for **1** at high dilution. In contrast to **1** the UV/Vis spectra of the metal complexes **2**–**4** in DMSO, DMF and MeCN are concentration-independent. Comparison of the UV/Vis spectra of the tris(catecholato)M complexes of **1** in DMSO with that of **1**$^{2-}$ shows a hypsochromic shift of the absorption maximum for M = Si^{IV} (**3**) (λ_{max} = 394 nm) over Al^{III} (**4**) (λ_{max} = 404 nm) to Ti^{IV} (**2**) (λ_{max} = 423 nm). The latter shows a maximum at about the same wavelength as the free ligand **1**$^{2-}$ (Figure 2). This behaviour reflects the different degree of ionicity in the M–O bond increasing from Si^{IV}–O over Al^{III}–O to Ti^{IV}–O. The high ionicity of the M–O bond concentrates charge on the catecholate oxygen atoms, which become stronger donors the more ionic the bond is. This results in an intraligand CT absorption as observed in, for example, other tris(catecholato)Ti^{IV} complexes.[26] Interestingly, the band width of this CT band is much broader for **2** than for **3** and **4**. Whether this effect has to do with diastereomeric mixtures or is due to electronic effects is presently unclear.

While the spectra of **2**–**4** do not vary much in DMSO, DMF and MeCN, further studies of their possible solvatochromism were hampered by the insolubility in less polar solvents. In MeOH decomposition of **3** was observed and free ligand **1** was formed.

The complexes **9** and **10** show a similar behaviour of the absorption spectra as the complexes **2**–**4** (Figure 3). The spectra of both compounds **9** and **10** are shifted batho-

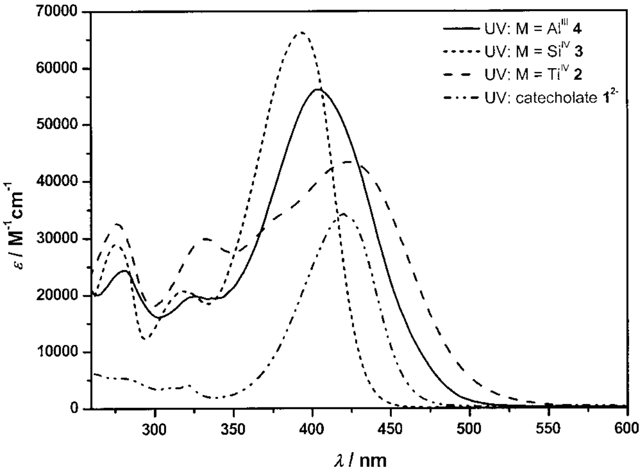


Figure 2. Absorption spectra of tris(catecholato)M complexes **2**–**4** and of catecholate **1**$^{2-}$ in DMSO.

chromically vs. the free ligand **8**. Even here the increasing ionic character of the M^{IV}–O bonding is responsible for the red shift of the absorption maximum of the Si^{IV} compound **10** vs. the Ti^{IV} compound **9**. In DMSO the band maximum for **9** is at λ_{max} = 460 nm and for **10** at λ_{max} = 442 nm. Surprisingly, even the absorption maximum of the Ti^{IV} complex **9** does not reach that of the free deprotonated ligand **8**$^{2-}$. This contrasts the behaviour of **2**. Neither the free ligand **8** nor the complexes themselves show fluorescence in DMSO, but their absorption is slightly solvatochromic (see Table 1). Ligand **8** shows, as for ligand **1**, a concentration-dependent deprotonation of the hydroxy groups to form the catecholate **8**$^{2-}$. Although the Ti^{IV} complex **9** has a higher stability compared to the Si^{IV} species **10**, we observe ligand exchange in methanol.

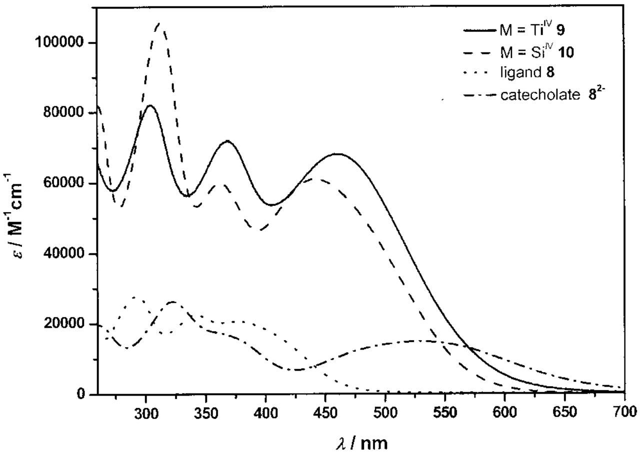


Figure 3. Absorption spectra of the tris(catecholato)M complexes **9**, **10** and the corresponding ligand **8** and catecholate **8**$^{2-}$ in DMSO.

The UV/Vis spectrum of **14** in DMSO is similar to the spectrum of **9** but has a maximum at λ_{max} = 391 nm which is blue-shifted vs. **9** due to the R_3N^+ electron acceptor that is weaker than the NO_2 group in **9** (Figure 4).

Table 1. UV/Vis data {λ_{max} [nm] (ε [M^{-1}cm^{-1}])} of ligands **1**, **8**, **13**, the corresponding catecholates **1**$^{2-}$, **8**$^{2-}$ and tris(catecholato)M^{III,IV} complexes **2**–**4**, **9**, **10**, **14**.

	DMSO	DMF	MeCN
1	340 (17100)		
1^{2-}	420 (34261)		
2	423 (43300)	426 (46400)	409 (41000)
3	394 (65200)	394 (69800)	378 (67000)
4	404 (56100)	408 (61800)	
8	377 (20500)		
8^{2-}	531 (14813)		
9	460 (68100)	463 (70900)	446 (71200)
10	442 (60900)	447 (62200)	429 (69100)
13	292 (21400)		
14	391 (63600)	397 (64800)	389 (65500)

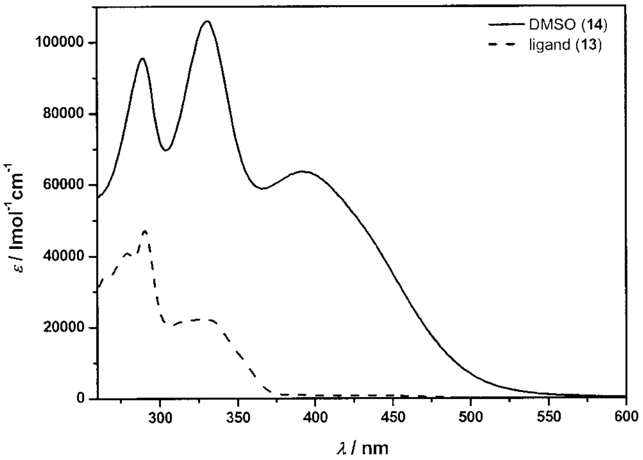


Figure 4. Absorption spectra of tris(catecholato)M complex **14** and ligand **13** in DMSO.

Conclusions

Although we could not measure the absorption spectra of the metal catecholates in solvents with strongly different polarity due to solubility/instability problems, the bathochromic shift of the lowest-energy transition for the ligands **1** and **8** on going from Si^{IV} via Al^{III} to Ti^{IV} complexes **2**–**4**, **9**, and **10** supports the assignment to an intraligand charge-transfer transition. The bathochromic shift of this transition reflects the increasing ionic character of the M–O bonding which in turn causes the catecholate oxygen atom to become a stronger donor in the Ti^{IV} complexes than in the Si^{IV} compounds. For this reason the spectroscopic properties of the Ti^{IV} complexes **2** and **9** approach those of the deprotonated free ligands **1**$^{2-}$ and **8**$^{2-}$. The higher energy transition of Ti^{IV} complex **14** compared to **9** reflects the much weaker electron acceptor strength of the trimethylammonio substituent compared to the nitro group.[33] The former substituent acts by a purely inductive (field) effect while in the latter mesomeric effects also play a role.

In conclusion, we were able to synthesise a series of octupolar chromophores and to characterise their linear optical properties. The metal complexes described in this paper can serve as reasonably stable substitutes for the much more sensitive free-ligand chromophores. Owing to their intense intraligand CT transitions these complexes might be good candidates as chromophores for first-order nonlinear applications.[34]

Experimental Section

General Remarks: All operations were performed under nitrogen or argon using standard Schlenk-line techniques. All reagents were purchased from commercial sources and used as received. Methyl 3-(3,4-dihydroxy)phenyl-2-propenoate (**1**),[35] 1,2-bis(*tert*-butyldimethylsilyloxy)-4,5-diiodobenzene (**5**),[31] 1-ethynyl-4-nitrobenzene (**6**),[36] and (4-ethynylphenyl)dimethylamine (**11**)[36] were prepared according to literature procedures.

Instrumental: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 FT NMR spectrometer. Elemental analyses were obtained from the Institut für Anorganische Chemie of the Universität Würzburg using an apparatus from Leco (CHNS-932). Infrared spectra were recorded in the range 4000–200 cm^{-1} as KBr pellets with a Jasco 410 FT-IR spectrometer. UV/Vis spectra were recorded with a Jasco V-570 UV/Vis/NIR spectrometer using Uvasol® solvents from Merck.

Dilithium Tris{4-[2-(methoxycarbonyl)ethenyl]-1,2-benzenediolato}-titanate(IV) (2): To a mixture of methyl 3-(3,4-dihydroxy)phenyl-2-propenoate (**1**; 250 mg, 1.28 mmol) and Li_2CO_3 (32.0 mg, 433 µmol) in dry MeOH (15 mL) $TiO(acac)_2$ (112 mg, 430 mmol) was added. The solution turned deep red and was stirred at room temperature for 24 h. The solvent was removed in vacuo, the red solid was dissolved in ethyl acetate and carefully covered with a layer of petroleum ether. The crystalline precipitate was filtered off, washed with petroleum ether and dried in vacuo to yield a red solid. Yield 72% (225 mg). ^{1}H NMR (250 MHz, [D$_6$]acetone, 25 °C): δ = 7.49 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, CH=C*H*), 6.72 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.2 Hz, 1 H, 5-H), 6.56 (d, $^4J_{HH}$ = 2.1 Hz, 1 H, 3-H), 6.23 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 6-H), 6.06 (d, $^3J_{HH}$ = 15.9 Hz, 1 H, C*H*=CH), 3.67 (s, 3 H, MeO) ppm. ^{13}C NMR (62.9 MHz, [D$_6$]acetone, 295 K): δ = 168.3, 160.6, 147.9, 125.0, 122.7, 112.2, 111.6, 109.9, 106.1, 51.2 ppm. $C_{30}H_{24}Li_2O_{12}Ti\cdot5H_2O$ (728.35): calcd. C 49.47, H 4.71; found C 49.69, H 5.13. IR (KBr): ṽ = 3052 (aryl-C–H), 3016 (w, aryl-C–H), 2975 (w, C–H), 1686 (m, C=O), 1624 (m), 1579 (w), 1486 (s), 1436 (m), 1261 (s, C–O), 1197 (w), 1118 (w), 1042 (vw), 977 (vw), 824 (w), 641 (m), 613 (w), 505 (w) cm^{-1}.

Bis(triethylammonium) Tris{4-[2-(methoxycarbonyl)ethenyl]-1,2-benzenediolato}silicate(IV) (3): To a mixture of methyl 3-(3,4-dihydroxy)phenyl-2-propenoate (**1**; 250 mg, 1.28 mmol) and Et_3N (119 mg, 908 µmol) in dry MeOH (5 mL) $Si(MeO)_4$ (63.9 mg, 409 µmol) was added. The solution turned yellow and was stirred at room temperature for 24 h. The solvent was removed in vacuo. The yellow solid was dissolved in dichloromethane and the solution added dropwise to petroleum ether. The precipitate was filtered off, washed with petroleum ether and dried in vacuo. Yield 88% (300 mg) of a yellow solid. ^{1}H NMR (250 MHz, [D$_4$]methanol, 25 °C): δ = 7.53 (d, $^3J_{HH}$ = 15.5 Hz, 1 H, CH=C*H*), 6.86 (s, 1 H, 3-H), 6.72 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 6-H), 6.53 (dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.2 Hz, 1 H, 5-H), 6.13 (d, $^3J_{HH}$ = 15.5 Hz, 1 H, C*H*=CH), 3.72 (s, 3 H, MeO), 3.08 (q, 12 H, $CH_3C\mathit{H}_2N$), 1.21 (t, 18 H, $C\mathit{H}_3CH_2N$) ppm. ^{13}C NMR (62.9 MHz, [D$_4$]methanol, 295 K): δ = 170.9, 156.5, 152.6, 149.5, 125.5, 123.6, 111.8, 111.2, 109.2, 50.8, 48.0 ($CH_3\mathit{C}H_2N$), 9.62 ($\mathit{C}H_3CH_2N$) ppm. $C_{42}H_{58}N_3O_{12}Si$ (811.00): calcd. C 62.20, H 7.21, N: 3.45; found C 61.32, H 7.15, N 3.46. IR (KBr): ṽ = 3057 (aryl-C–H), 3019 (w, aryl-C–H), 2986 (w, C–H), 2949 (w, C–H), 1697 (m, C=O), 1623 (m), 1590 (m), 1497 (s), 1447 (m), 1354 (w), 1259 (s, C–O), 1157 (s), 1117 (m), 1035 (vw), 985 (vw), 926 (vw), 835 (m), 790 (w), 694 (m), 578 (vw), 523 (w) cm^{-1}.

Trilithium Tris{4-[2-(methoxycarbonyl)ethenyl]-1,2-benzenediolato}-aluminate(III) (4): To a mixture of methyl 3-(3,4-dihydroxy)phenyl-2-propenoate (**1**; 300 mg, 1.54 mmol) and Li_2CO_3 (56.2 mg, 758 µmol) in dry MeOH (15 mL) $Al(acac)_3$ (165 mg, 509 µmol) was added. The solution turned yellow and was stirred at room temperature for 24 h. The solvent was removed in vacuo, the remaining yellow solid was suspended in hot ethyl acetate and filtered off. The precipitate was washed twice with hot ethyl acetate and dried in vacuo. Yield 84% (268 mg) of a yellow solid. ^{1}H NMR (250 MHz, [D$_4$]methanol, 25 °C): δ = 7.49 (d, $^3J_{HH}$ = 15.4 Hz, 1 H, CH=C*H*), 6.78 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 3-H), 6.57 (dd, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.8 Hz, 1 H, 5-H), 6.42 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 6-H), 6.00 (d, $^3J_{HH}$ = 15.5 Hz, 1 H, C*H*=CH), 3.70 (s, 3 H, MeO) ppm. ^{13}C NMR (62.9 MHz, [D$_4$]methanol, 295 K): δ = 171.3, 162.0, 156.4, 150.3, 123.3, 123.0, 112.9, 110.0, 108.5, 51.6 ppm. $C_{30}H_{24}AlLi_3O_{12}\cdot5H_2O$ (714.34): calcd. C 50.44, H 4.80; found C 50.79, H 4.84. IR (KBr): ṽ = 3054 (vw, aryl-C–H), 2984 (w, C–H), 1685 (m, C=O), 1622 (m), 1582 (m), 1497 (s), 1437 (m), 1346 (vw), 1269 (s, C–O), 1199 (m), 1166 (m), 1120 (w), 1042 (vw), 980 (w), 929 (vw), 827 (w), 784 (vw), 655 (w), 616 (w) cm^{-1}.

1,2-Bis(*tert*-butyldimethylsilyloxy)-4,5-bis[2-(4-nitrophenyl)ethynyl]-benzene (7): To a mixture of 4,5-bis(*tert*-butyldimethylsilyloxy)-1,2-diiodobenzene (**5**; 189 mg, 320 µmol), $(PPh_3)_2PdCl_2$ (24.0 mg, 34.2 µmol) and Cu^II (4.00 mg, 21.0 µmol) in dry Et_2NH (5 mL) was added 1-ethynyl-4-nitrobenzene (**6**; 100 mg, 680 µmol). The red solution was heated to 60 °C for 1 h, cooled to room temperature and the solvent was evaporated in vacuo. The remaining black solid was purified by flash chromatography on silica gel (dichloromethane/petroleum ether, 2:3) to yield a yellow solid. The solid was dissolved in dichloromethane and the solution added dropwise to petroleum ether. The dichloromethane was removed in a rotary evaporator, the precipitate was filtered and dried in vacuo. Yield 75% (163 mg) of a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 8.22 (AA′, 4 H), 7.65 (BB′, 4 H), 7.03 (s, 2 H, 3-H, 6-H), 1.01 [s, 18 H, $(C\mathit{H}_3)_3CSi$], 0.26 [s, 12 H, $(C\mathit{H}_3)_2Si$] ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 295 K): δ = 149.5, 148.2, 133.2, 130.7, 125.3, 124.8, 119.6, 93.3, 91.7, 26.2, 19.2, –3.85 ppm. $C_{34}H_{40}N_2O_6Si_2$ (677.24): calcd. C 64.94, H 6.41, N 4.45; found C 64.69, H 6.24, N 4.52. IR (KBr): ṽ = 3041 (vw, aryl-C–H), 2951 (w, C–H), 2930 (w, C–H), 2857 (w, C–H), 2204 (vw, C≡C), 1592 (m), 1536 (w), 1510 (s, NO_2), 1410 (w), 1345 (w), 1336 (s, NO_2), 1256 (m), 1213 (vw), 1105 (w), 1083 (w), 939 (m), 886 (vw), 871 (w), 848 (m), 843 (m), 783 (w), 748 (vw), 684 (vw) cm^{-1}.

1,2-Dihydroxy-4,5-bis[2-(4-nitrophenyl)ethynyl]benzene (8): To a solution of 1,2-bis(*tert*-butyldimethylsilyloxy)-4,5-bis[2-(4-nitrophenyl)ethynyl]benzene (**7**; 95.0 mg, 140 µmol) in dry THF (10 mL) tetrabutylammonium fluoride (101 mg, 386 µmol, 1 M solution in THF) was added. The deep purple solution was stirred at room temperature for 30 min and a cold H_3PO_4 solution (30 mL, 1 M) was added. The mixture was extracted with Et_2O (3 × 30 mL). The organic phases were combined, dried with Na_2SO_4 and the solvent was removed in vacuo. The remaining brown solid was purified by flash chromatography on silica gel (ethyl acetate/*n*-hexane/CH_3COOH, 10:25:1) to yield an orange solid. The solid was dissolved in ethyl acetate and the solution added dropwise to *n*-hexane. The precipitate was filtered off and dried in vacuo. Yield 98% (55.0 mg) of an orange solid. ^{1}H NMR (250 MHz, [D$_6$]acetone, 25 °C): δ = 8.31 (AA′, 4 H), 7.84 (BB′, 4 H), 7.44 (br., 2 H, HO), 7.17 (s, 2 H, 3-H, 6-H) ppm. ^{13}C NMR (62.9 MHz, [D$_6$]acetone, 295 K): δ = 148.0, 147.9, 133.1, 131.0, 124.8, 119.7, 118.0, 94.2, 90.8 ppm. $C_{22}H_{12}N_2O_6 \cdot H_2O$ (418.35): calcd. C 63.16, H 3.37, N 6.70; found C 63.51, H 3.49, N 6.41. IR (KBr): $\tilde{\nu}$ = 3480 (br., O–H), 3046 (vw, aryl-C–H), 2204 (m, C≡C), 1590 (s), 1508 (s, NO_2), 1441 (vw), 1349 (s, NO_2), 1308 (m), 1261 (w), 1182 (w), 1145 (w), 1074 (vw), 848 (m), 749 (w), 686 (vw) cm^{-1}.

Dilithium Tris{4,5-bis[2-(4-nitrophenyl)ethynyl]-1,2-benzenediolato}-titanate(IV) (9): To a mixture of 1,2-dihydroxy-4,5-bis[2-(4-nitrophenyl)ethynyl]benzene (**8**; 50.0 mg, 125 µmol) and Li_2CO_3 (3.10 mg, 41.9 µmol) in dry MeOH (10 mL) $TiO(acac)_2$ (10.9 mg, 41.5 µmol) was added. The solution turned deep red and was stirred at room temperature for 24 h. The solvent was removed in vacuo, the red solid was dissolved in THF and Et_2O and carefully covered with a layer of petroleum ether. Overnight a red solid crystallised which was filtered off and recrystallised from MeCN. Yield 88% (49.0 mg) of a red solid. ^1H NMR (250 MHz, [D_4]methanol, 25 °C): δ = 8.25 (AA′, 12 H), 7.68 (BB′, 12 H), 6.62 (s, 6 H, 3-H, 6-H) ppm. ^{13}C NMR (62.9 MHz, [D_4]methanol, 295 K): δ = 161.6, 147.6, 132.5, 132.2, 124.5, 116.4, 115.4, 96.7, 89.9 ppm. $C_{66}H_{36}Li_2N_6O_{18}Ti \cdot 4H_2O$ (1328.86): calcd. C 59.66, H 2.88, N 6.32; found C 59.41, H 2.58, N 6.16. IR (KBr): $\tilde{\nu}$ = 3056 (vw, aryl-C–H), 2196 (m, C≡C), 1592 (m, NO_2), 1509 (m), 1498 (m), 1477 (m), 1341 (s, NO_2), 1241 (s, C–O), 1106 (w), 887 (w), 850 (w), 792 (w), 748 (w), 705 (vw), 687 (vw), 613 (w) cm^{-1}.

Bis(triethylammonium) Tris{4,5-bis[2-(4-nitrophenyl)ethynyl]-1,2-benzenediolato}silicate(IV) (10): To a mixture of 1,2-dihydroxy-4,5-bis[2-(4-nitrophenyl)ethynyl]benzene (**8**; 100 mg, 249 µmol) and Et_3N (16.2 mg, 124 µmol) in dry MeCN (10 mL) a 1 M solution of $Si(MeO)_4$ (12.1 mg, 77.4 µmol) in dry MeCN was added. The solution turned orange and was stirred at room temperature for 24 h. Overnight a solid precipitated which was filtered off, washed with MeCN and dried in vacuo. Yield 78% (76.0 mg) of an orange solid. ^1H NMR (250 MHz, [D_6]DMSO, 25 °C): δ = 8.26 (AA′, 12 H), 7.73 (BB′, 12 H), 6.55 (s, 6 H, 3-H, 6-H), 3.06 (q, 12 H, CH_3CH_2N), 1.16 (t, 18 H, CH_3CH_2N) ppm. ^{13}C NMR (62.9 MHz, [D_6]DMSO, 295 K): δ = 154.6, 146.0, 131.7, 130.5, 124.1, 112.8, 111.9, 97.1, 88.9, 45.8, 8.8 ppm. $C_{78}H_{64}N_8O_{18}Si$ (1429.5): calcd. C 65.54, H 4.51, N 7.84; found C 64.13, H 4.38, N 7.56. IR (KBr): $\tilde{\nu}$ = 3071 (w, C–H-aryl), 2197 (m, C≡C), 1591 (s, NO_2), 1498 (s), 1384 (w), 1340 (s, NO_2), 1244 (s, C–O), 1173 (vw), 1105 (w), 1073 (vw), 891 (w), 852 (w), 795 (w), 748 (w), 711 (vw), 687 (vw), 655 (w), 596 (vw), 565 (vw) cm^{-1}.

1,2-Bis(*tert*-butyldimethylsilyloxy)-4,5-bis{2-[4-(dimethylamino)-phenyl]ethynyl}benzene (12): To a mixture of 4,5-bis(*tert*-butyldimethylsilyloxy)-1,2-diiodobenzene (**5**; 189 mg, 320 µmol), $(PPh_3)_2PdCl_2$ (24.0 mg, 34.2 µmol) and $Cu^I I$ (4.00 mg, 21.0 µmol) in dry Et_2NH (5 mL) (4-ethynylphenyl)dimethylamine (**11**; 100 mg, 680 µmol) was added. The red solution was heated to 50 °C for 24 h, cooled to room temperature and the solvent was evaporated in vacuo. The remaining brown solid was purified by chromatography on Al_2O_3 (neutral, act. V; dichloromethane/petroleum ether, 1:9) to yield a colourless solid. Yield 78% (156 mg) of a colourless solid. ^1H NMR (250 MHz, [D_6]acetone, 25 °C): δ = 7.38 (AA′, 4 H), 6.99 (s, 2 H, 3-H, 6-H), 6.72 (BB′, 4 H), 2.99 (s, 12 H, Me_2N), 1.02 [s, 18 H, $(CH_3)_3CSi$], 0.28 [s, 12 H, $(CH_3)_2Si$] ppm. ^{13}C NMR (62.9 MHz, [D_6]acetone, 25 °C): δ = 151.6, 148.0, 133.6, 124.7, 121.2, 113.1, 111.2, 94.5, 87.3, 40.5, 26.6, 19.4, –3.50 ppm. $C_{38}H_{52}N_2O_2Si_2$ (625.02): calcd. C 73.03, H 8.39, N 4.48; found C 72.88, H 8.19, N 4.58. IR (KBr): $\tilde{\nu}$ = 3045 (vw, aryl-C–H), 2953 (w, C–H), 2929 (m, C–H), 2885 (w, C–H), 2857 (m, N–Me), 2199 (vw, C≡C), 1608 (s), 1523 (s), 1496 (w), 1362 (s), 1254 (m), 1187 (w), 1136 (w), 929 (m), 887 (vw), 861 (w), 840 (m), 816 (w), 782 (w) cm^{-1}.

1,2-Bis(*tert*-butyldimethylsilyloxy)-4,5-bis{2-[4-(trimethylammonio)-phenyl]ethynyl}benzene Diiodide (13): To a solution of 1,2-bis(*tert*-butyldimethylsilyloxy)-4,5-bis{2-[4-(dimethylamino)phenyl]-ethynyl}benzene (**12**; 1.45 g, 2.31 mmol) in THF (20 mL) methyl iodide (5 mL) was added. The reaction mixture was sealed in a Schlenk tube and heated to 55 °C for 4 d. Excess methyl iodide and the solvent were removed in vacuo. The light yellow solid was dissolved in acetone by heating the mixture to 40 °C, *n*-hexane was added and the acetone was removed in a rotary evaporator. The precipitate was filtered off and washed twice with *n*-hexane to yield a colourless solid. Yield 86% (1.78 g). ^1H NMR (250 MHz, [D_6]-DMSO, 25 °C): δ = 8.06–8.03 (4 H), 7.79–7.74 (4 H), 7.11–7.00 (2 H, 3-H, 6-H), 3.64 (18 H, Me_3N), 0.98–0.83 [18 H, $(CH_3)_3CSi$], 0.25 to –0.04 [12 H, $(CH_3)_2Si$] ppm. ^{13}C NMR (62.9 MHz, [D_6]-DMSO, 25 °C): δ = 147.78, 146.78, 132.51, 132.42, 132.34, 132.24, 124.10, 123.91, 121.29, 121.24, 118.10, 90.26, 89.60, 56.41, 56.34, 25.50, 25.32, 25.26, 18.15, 18.13, 17.72, –3.24, –4.26, –4.54 ppm. $C_{40}H_{58}I_2N_2O_2Si_2$ (908.89): calcd. C 52.86, H 6.43, N 3.08; found C 52.59, H 6.18, N 3.11. IR (KBr): $\tilde{\nu}$ = 3013 (vw, C–H-aryl), 2955 (w, C–H), 2929 (w, C–H), 2885 (vw, C–H), 2857 (w, N–Me), 2210 (vw, C≡C), 1532 (m), 1513 (s), 1492 (m), 1471 (w), 1407 (w), 1357 (m), 1254 (s), 1117 (vw), 1082 (vw), 1013 (vw), 934 (s), 887 (w), 840 (s), 804 (w), 783 (m), 687 (vw), 564 (vw) cm^{-1}.

Tris(4,5-bis{2-[4-(trimethylammonio)phenyl]ethynyl}-1,2-benzenediolato)titanium(IV) Tetraiodide (14): To a solution of 1,2-bis(*tert*-butyldimethylsilyloxy)-4,5-bis{2-[4-(trimethylammonio)phenyl]-ethynyl}benzene diiodide (**13**; 200 mg, 220 µmol) in dry MeOH (13 mL) was added nBu_4NF (151 mg, 578 µmol, 1 M solution in THF) followed by $TiO(acac)_2$ (19.2 mg, 73.2 µmol). The solution turned red and was stirred at room temperature for 24 h. The orange precipitate was filtered off and washed carefully with MeOH. The solid was suspended in MeOH (15 mL) and the suspension added dropwise to a concd. solution of $NH_4(PF_6)$ in MeOH (10 mL). The precipitate was filtered off and the procedure was repeated twice to yield an orange solid. Yield 86% (114 mg). ^1H NMR (250 MHz, [D_6]DMSO, 25 °C): δ = 7.98 (AA′, 12 H), 7.70 (BB′, 12 H), 6.30 (s, 6 H, 3-H, 6-H), 3.62 (s, 18 H, Me_3N) ppm. ^{13}C NMR (62.9 MHz, [D_6]DMSO, 25 °C): δ = 162.1, 146.0, 132.0, 125.4, 121.1, 113.4, 93.4, 88.3, 56.4 ppm. $C_{84}H_{90}I_4N_6O_6Ti \cdot 4H_2O$ (1901.19): calcd. C 53.07, H 4.87, N 4.42; found C 53.08, H 4.98, N 4.42. IR (KBr): $\tilde{\nu}$ = 3014 (vw, C–H-aryl), 2955 (w, C–H), 2929 (w, C–H), 2885 (w, C–H), 2857 (w, N–Me), 2198 (w, C≡C), 1508 (w), 1479 (s), 1413 (w), 1369 (m), 1278 (w), 1244 (s, C–O), 1200 (w), 1113 (w), 1011 (vw), 955 (vw), 936 (w), 884 (w), 844 (m), 798 (w), 635 (m), 565 (m), 502 (m) cm^{-1}.

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