The Introduction of OH and COOH Groups into 4*H*-Imidazoles: Water-Soluble Functional Dyes and Quinomethides

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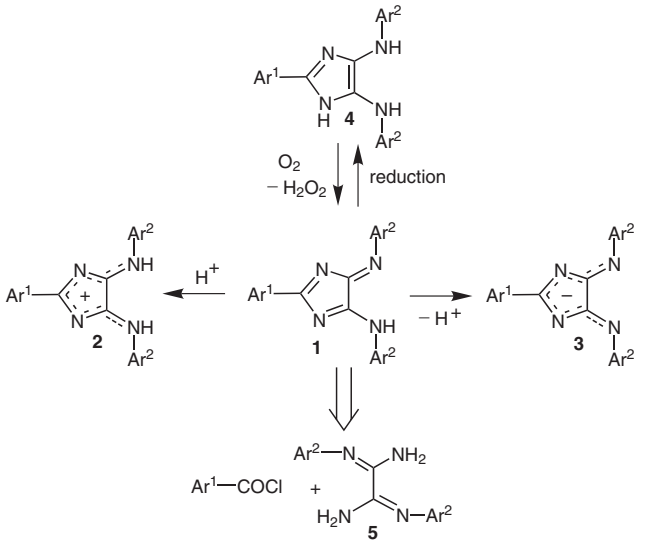
Abstract: Water-soluble 4*H*-imidazoles, which represent redox- as well as pH-switchable functional dyes, are synthesized via a novel procedure. In a smooth reaction, phthalic anhydride reacts with oxalic acid amidine **5** yielding 4*H*-imidazole **1a**. Analogously, but in lower yields, naphthalene-1,8-dicarboxylic anhydride and 2-sulfobenzoic anhydride can be transformed into 4*H*-imidazoles **1b**,**c**. 4-Hydroxybenzoic acids do not form the expected 4*H*-imidazoles, which possess hydroxyaryl substructures. However, in the course of the cyclization–long-range prototropism sequence, the new quinomethides **7a–c** were obtained. This sequence could be adapted successfully for the synthesis of corresponding thioxo derivatives **7d**. The water-soluble 4*H*-imidazoles **1a–c** as well as quinomethides of type **7** proved to be multifunctional and switchable dyes. They show acidochromism and in addition, can be transformed into fluorescent leuco forms, which reoxidize when exposed to air.

Key words: heterocycles, carboxylic acids, quinomethides, functional dyes, tautomerism

During the last few years there has been an exciting variety of developments in new technologies using functional dyes. In addition to their features as functional materials, modern chromophores and fluorophores are mainly used in medicinal diagnostics, biology, and biochemistry as marker substances and sensors for biological active molecules. Therefore, the water solubility of these derivatives is a major requirement.

4*H*-Imidazoles **1**, developed in our group, represent a new class of functional dyes; these cyclic merocyanines are pH-sensitive and can be transformed by protonation/deprotonation into chromophores that absorb at longer wavelengths (cyanines **2**/azaoxonoles **3**, Scheme 1).[1] Recently, palladium complexes that contain merocyanine-like 4*H*-imidazoles as ligands have been synthesized. These complexes can be regarded as new functional dyes as well as deeply colored and redox active metallacycles that display catalytic activity.[2] However, the most important feature is their reversible redox behavior. They can easily be reduced giving derivatives of 4,5-diaminoimidazole **4** (Scheme 1) as leuco forms.[3,4]

The latter, 4,5-diaminoimidazoles **4**, are not only highly substituted heteroaromatics, but also cyclic versions of



Scheme 1 4*H*-Imidazoles; acidochromic and redox switchable functional dyes

electron-rich olefins that immediately reoxidize in the presence of oxygen.[4] When the reduction is carried out in aqueous solution, e.g. by sodium dithionite, exactly one equivalent of hydrogen peroxide forms upon reoxidation. This redox reaction of 4*H*-imidazoles is connected with a drastic color alteration making them attractive for applications in molecular switches, markers, and others. The water solubility of these derivatives can only be realized thus far by the use of co-solvents, therefore we are interested in the synthesis of such species that display water solubility.

Based on earlier findings, functional groups (e.g., halo, CF_3, or COOR) can easily be integrated into the peripheral aryl substituents of their five-ring system.[5] Due to the high reactivity of XH groups in the synthesis of ethers or esters, in connection with characteristic features such as tautomerism and absorption/chemisorption on surfaces, our additional aim was the introduction of OH/SH groups.

4*H*-Imidazoles can be synthesized by different synthetic processes.[5–9] In our case, the cycloacylation of oxalamidines **5**, which tolerate a broad variability of substituents in the 2-position, was the method of choice.[9] Instead of acyl chlorides, carboxylic anhydrides were used. Firstly, phthalic anhydride was tested as model substance (Scheme 2). Upon addition of the carboxylic acid derivative to a solution of the deprotonated oxalamidine **5a**, the

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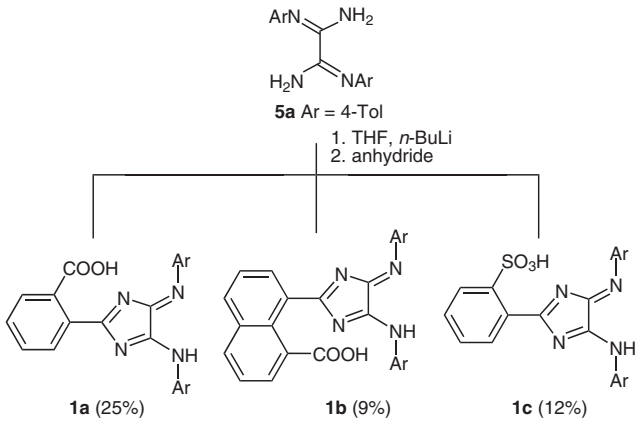


Scheme 2 Synthesis of carboxy/sulfo-functionalized 4*H*-imidazoles

color of the reaction mixture immediately turned from yellow to orange-red. The workup was optimized as follows: the separation of the formed lithium salts was realized by washing the dissolved (CH_2Cl_2 or $CHCl_3$) product with water, subsequently the 4*H*-imidazole was purified by column chromatography. While the organic layer mostly contained unreacted starting material **5a** and *N*-tolylphthalimide as a byproduct, the 4*H*-imidazole **1a** was extracted from the aqueous layer with dichloromethane by addition of a small amount of acetic acid.

Other anhydrides were tested in the same manner, whereby only naphthalene-1,8-dicarboxylic anhydride and 2-sulfobenzoic anhydride gave the corresponding 4*H*-imidazoles **1b** and **1c** in appreciable yields. 3-Nitronaphthalene-1,8-dicarboxylic anhydride and benzene-1,2,4,5-tetracarboxylic dianhydride proved to be reactive; however, inseparable mixtures of isomers were obtained. Naphthalene-1,4,5,8- and perylene-3,4,9,10-tetracarboxylic dianhydrides gave no results due to their low solubility; the corresponding 4*H*-imidazoles could only be detected in trace amounts by TLC. In addition, as in the case of maleic anhydride, the formation of cyclic imides is favored here.[10–14]

All 4*H*-imidazoles **1a–c** are highly soluble in water showing strong hydrophilicity, which makes these derivatives insoluble even in dried organic solvents. Reduction with aqueous sodium dithionite solution yields yellow-green-ish fluorescent 1*H*-imidazoles **4** (Scheme 1), which quickly reoxidize when exposed to air. As depicted in Figure 1 the well-separated graphs of both species in the UV/Vis-spectra allow their quantification. In case of reduction/reoxidation of derivative **1a/4a**, an isosbestic point at 431 nm was obtained.

Whereas 4*H*-imidazoles **1a–c** reacted with aqueous alkali hydroxides to give deep purple carboxylates/sulfonates, upon addition of hydrochloric acid fast hydrolytic decomposition (pH <5.5) with decolorization takes place.

3,5-Di-*tert*-butyl-4-hydroxybenzoic acid and 4-hydroxybenzoic acid were chosen as starting materials for the synthesis of 4-hydroxyaryl-substituted 4*H*-imidazoles because of their commercial availability. Both acids can be transformed nearly quantitatively into the corresponding acid chlorides **6a**,**b** upon treatment with thionyl chloride/oxalyl chloride,[15] which were then cyclized with oxalamidines **5a**,**b** according to known procedures[7] to give deep red products in moderate yields. Elemental analyses and MS/NMR data confirmed the structure of quinomethides[16] **7** for the new products obtained. As shown in Scheme 3, based on the existence of 4-OH groups the assignment of different tautomeric forms is possible. The well-resolved ^{1}H NMR spectra measured at different temperatures show that only one of three species is predominant in solution. The existence of tautomeric form **7″** could be excluded by IR spectroscopy. Instead of characteristic broad absorptions in the frequency range of OH groups, a strong absorption band for the carbonyl group at about 1730 cm^{-1} was detected.

The spectroscopic evidence was supported by the fact that derivative **7** showed no tendency to form highly fluorescent boracycles[17] upon treatment with boron compounds, e.g. $BF_3{\cdot}OEt_2$. Furthermore, all attempts to establish prototropic form **7′** by using cyclization reactions (trialkyl orthoformate or triphosgene) were unsuccessful. This observation is in accordance with results obtained for vinylogous tetraazafulvalenes, where these cyclization reactions completely failed.[18] All these spectral and chemical findings clearly underline the existence of a structure in accord with **7** (Scheme 3).

For a better understanding of this type of prototropism ('long-range-prototropism'), 4-mercaptobenzoic acid was integrated into this cyclization reaction. Thus, starting

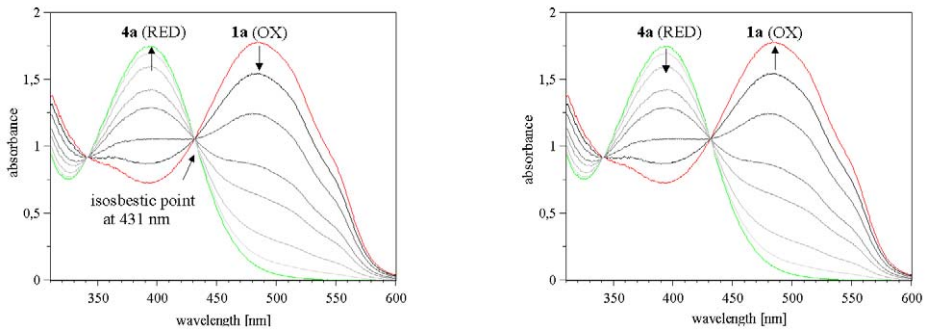
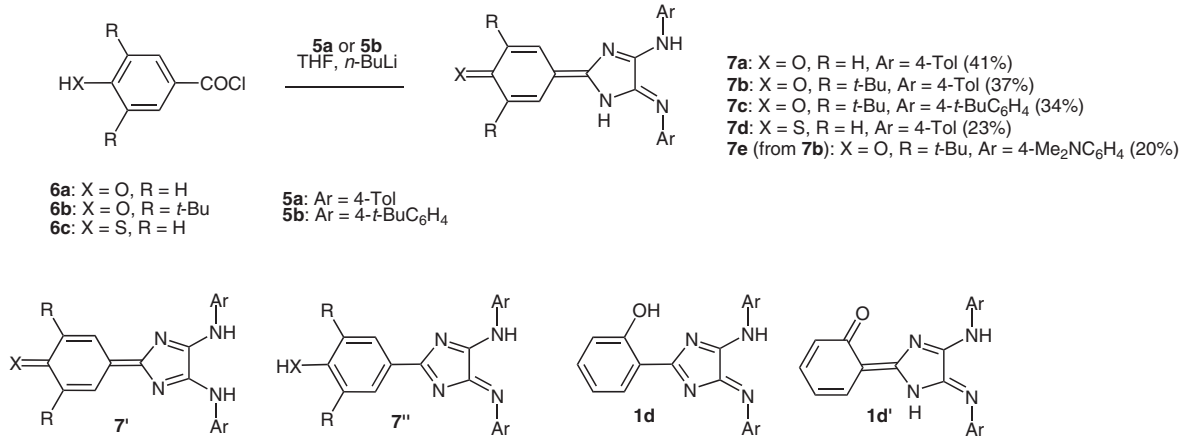
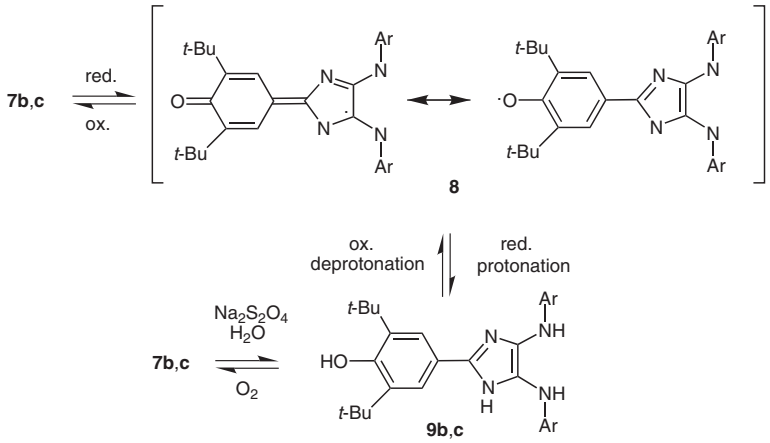


Figure 1 Reduction of **1a** and reoxidation of **4a** (Ar^1 = 4-Tol, Ar = 2-$HO_2CC_6H_4$)



Scheme 3 Synthesis of quinomethides **7**



Scheme 4 Reduction of quinomethides **7**

from the chloride **6c**, a deeply colored product was isolated with spectral data in accordance with structure **7d**.

In addition to the derivatives described above, the formerly synthesized 4*H*-imidazole **1d**[7] was included in the following considerations. In contrast to its 4-substituted derivative, this 4*H*-imidazole does not show any tendency to tautomerize into *ortho*-quinomethide **1d′**.

The different behavior of such derivatives with respect to tautomerization processes shows that exclusively XH substituents in the 4-position effected the transformation into quinomethides of type **7**. In the course of the proton shift, the electronic nature partially changes, meaning that the aryl subunit was oxidized, while the 4*H*-imidazole nuclei was reduced.[19] Similar transformations have been observed on substituted benzothiazoles of 7-hydroxy-1,6-methano[10]annulenes.[20]

The spectroscopic properties of derivatives **7** slightly vary from those of 'normal' aryl-substituted 4*H*-imidazoles. Despite the non-equivalence of the arylamino/arylimino substituents resulting in different signal sets, only two doublets for the aromatic protons were detected. This characteristic feature is explained by very fast intermolecular proton-exchange processes. According to structure **7** (Scheme 3), the IR spectra show two NH absorptions, however only one was detected for the C=O/C=S group. The absorption maxima of the deep red colored solutions of derivatives **7a–d** lie in the range of ~520 nm with extinction coefficients higher than 4.0. Compared to the 4*H*-imidazoles prepared earlier,[1,7,8] tautomerization into quinomethides of type **7** causes a bathochromic shift of the longest wavelength absorption band. While the chromophoric system of 4*H*-imidazoles **1** is based on a diazapentamethine–merocyanine, that of quinomethides **7a–e** was extended to a diazaheptamethine–merocyanine.

Generally, derivatives **7** show reactivity comparable to their parent compounds. Thus, derivative **7b** can be converted into the deep purple **7e** (X = O, R = *t*-Bu, Ar = 4-$Me_2NC_6H_4$) by transamination[7,8] with 4-(dimethyl)-1,2-phenylenediamine in the presence of catalytic amounts of *p*-toluenesulfonic acid.

Being amphoteric heterocycles, derivatives of type **7** react with acids as well as with bases to yield salts. The different colors of their solutions are caused by alteration of the chromophoric system. Whereas deprotonation of **7b** with butyllithium gives deep purple (aza)oxonoles of type **3** (λ = 539 nm), the transition from merocyanine to cyanine **2** in case of protonation resulted in a bathochromic shift of 70–100 nm. The possible application of 4*H*-imidazoles as

quantitative pH-sensor systems has already been discussed.[1] The reduction of the quinomethides **7** proceeds in a similar manner as for 4*H*-imidazoles (Scheme 4).[3] Compared with earlier data, very high semiquinomethide **8** formation constants ($K_{SEM} = 3.6 \times 10^{13}$ to 3.8×10^{14}) were ascertained. Most likely, this increasing rate is caused by the localization of the radical electron at the oxygen atom. In case of **8b**, better stabilization by steric effects can additionally be discussed.[1,21,22] However, the kinetic stability of the radical **8b** derived from **7b** is very low, so that no signals could be detected by ESR measurements. The reduction of **7b**,**c** with an aqueous solution of sodium dithionite yields yellow, greenish fluorescent and oxygen-sensitive 1*H*-imidazoles **9b**,**c** in a single step, which quickly reoxidize upon contact with air.

A novel synthetic route to water-soluble 4*H*-imidazoles **1a–c** starting from aromatic carboxylic acid anhydrides was developed. These derivatives are fully reversible two-step redox systems, evidenced by UV/Vis and electrochemical measurements. Therefore they might be applicable as functional dyes for the quantification of biochemical redox processes. A further interesting feature is their long wavelength absorption ($\lambda_{max} = 480$ to 530 nm) connected with high extinction coefficients (log ε >4).

Starting from benzoic acids which possess XH groups in the 4-position novel quinomethides **7** were synthesized. In addition to their halochromism, they proved to be reversible two-step redox systems with high K_{SEM} values.

All reactions were monitored by TLC, carried out on 0.25 mm Merck silica gel plates ($60F_{254}$) using UV light. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX 400 or Bruker AC 250 spectrometer. Melting points are measured with a Galen TM 3 apparatus and are uncorrected. UV-VIS spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. MS spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Electrochemical measurements were carried out with a Metrohm 663VA Stand using Hg or Pt electrodes and Bu_4NPF_6 as conductive salt.

Carboxy/Sulfo-Substituted 4*H*-Imidazoles 1; General Procedure

Bis(tolyl)oxalamidine **5** (266 mg, 1.0 mmol) dissolved in anhyd THF (20 mL) was deprotonated with 1.6 M BuLi in THF (1.3 mL, 2.1 mmol) at r.t. to obtain a yellow-orange soln of amidinate. After addition of the corresponding acid anhydride (0.7 mmol), the mixture immediately turned orange-red. The mixture was refluxed for 2–4 h until completion, then cooled to r.t., evaporated to dryness, and the residue was dissolved in CH_2Cl_2. The organic layer was washed with H_2O to extract the crude product and inorganic salts. The 4*H*-imidazoles **1** were isolated by extraction of the aqueous layer with CH_2Cl_2 with the addition of AcOH (1–2 drops). The organic layers were dried (anhyd Na_2SO_4) and filtered and the solvent was evaporated under reduced pressure to give the orange-red 4*H*-imidazoles **1**.

2-[5-(4-Tolylamino)-4-(4-tolylimino)-4*H*-imidazol-2-yl]benzoic Acid (1a)

Orange-red powder; yield: 25%; mp > 200 °C (dec.).

IR (ATR): 1707, 3262 (br), 3428 cm^{-1}.

^{1}H NMR (250 MHz, THF-d_8/D_2O): δ = 2.17 (s, 6 H), 6.98 (d, ^3J = 8.3 Hz, 4 H), 7.20–7.35 (m, 2 H), 7.68–7.80 (m, 6 H).

^{13}C NMR (62 MHz, THF-d_8/D_2O): δ = 18.1, 119.3, 126.9, 127.1, 127.6, 129.5, 134.5, 135.2, 135.6, 145.5, 147.7, 163.6, 168.4, 174.7.

MS (DEI): *m*/*z* (%) = 91 (58), 106 (100), 133 (46), 149 (29), 167 (32), 237 (41), 266 (76), 351 (7), 396 (68) [M]$^+$, 397 (25) [M + H]$^+$.

UV/Vis (THF–H_2O, 1:1): λ_{max} (log ε) = 448 (4.3), 482 nm (4.1).

Anal. Calcd for $C_{24}H_{20}N_4O_2$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.82; H, 5.15; N, 14.10.

8-[5-(4-Tolylamino)-4-(4-tolylimino)-4*H*-imidazol-2-yl]-1-naphthoic Acid (1b)

Red powder; yield: 9%.

IR (ATR): 1698, 3326 (br), 3679 cm^{-1}.

^{1}H NMR (250 MHz, THF-d_8/D_2O): δ = 2.28 (s, 6 H), 6.80 (d, ^3J = 8.2 Hz, 4 H), 6.91 (d, ^3J = 8.2 Hz, 1 H), 7.09 (d, ^3J = 8.2 Hz, 4 H), 7.28 (d, ^3J = 8.2 Hz, 1 H), 7.39 (t, ^3J = 8.3 Hz, 1 H), 7.53 (t, ^3J = 8.2 Hz, 1 H), 7.65 (d, ^3J = 8.3 Hz, 1 H), 7.89 (d, ^3J = 8.3 Hz, 1 H), 8.04 (s, 1 H).

^{13}C NMR (62 MHz, THF-d_8/D_2O): δ = 18.1, 121.8, 126.2, 126.7, 127.1, 127.6, 128.0, 129.1, 129.5, 134.4, 134.9, 135.0, 135.6, 145.5, 147.7, 163.2, 167.6, 176.7.

MS (FAB in nba): *m*/*z* (%) = 235 (100), 259 (29), 265 (44), 313 (69), 349 (48), 466 (10) [M]$^+$.

UV/Vis (THF–H_2O, 1:1): λ_{max} (log ε) = 430 (4.2), 500 nm (4.1).

Anal. Calcd for $C_{28}H_{22}N_4O_2$: C, 75.32; H, 4.97; N, 12.55. Found: C, 75.43; H, 5.05; N, 12.60.

2-[5-(4-Tolylamino)-4-(4-tolylimino)-4*H*-imidazol-2-yl]benzenesulfonic Acid (1c)

Red powder; yield: 12%.

IR (ATR): 1606, 3306 (br), 3428 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6/D_2O): δ = 2.17 (s, 6 H), 6.56 (d, ^3J = 8.0 Hz, 1 H), 6.81 (d, ^3J = 8.0 Hz, 1 H), 7.34 (d, ^3J = 8.5 Hz, 4 H), 7.4–7.5 (m, 2 H), 7.71 (d, ^3J = 8.0 Hz, 4 H).

^{13}C NMR (62 MHz, acetone-d_6/D_2O): δ = 22.3, 116.0, 120.2, 124.4, 126.9, 127.1, 127.4, 129.1, 129.5, 130.6, 138.5, 139.2, 146.4, 176.3.

MS (FAB in nba): *m*/*z* (%) = 207 (45), 233 (50), 248 (51), 267 (100), 293 (44), 333 (67), 347 (25), 359 (19), 376 (29), 401 (21), 432 (12) [M]$^+$.

UV/Vis (THF–H_2O, 1:1): λ_{max} (log ε) = 462 nm (4.0).

Anal. Calcd for $C_{23}H_{20}N_4O_3S$: C, 63.87; H, 4.66; N, 12.95; S, 7.41 Found: C, 63.90; H, 4.72; N, 13.04; S, 7.34.

Quinomethides 7; General Procedure

The corresponding oxalamidine **5** (1.0 mmol) was dissolved in anhyd THF (30 mL) under an argon atmosphere. To this soln 1.0 M BuLi in *n*-hexane (2.0 mL) was added and the mixture was stirred at r.t. for 10 min. Then, the corresponding acid chloride **6** (1.0 mmol) was added dropwise to the mixture, which was finally heated under reflux for 3 h. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, toluene–acetone, 10:1).

4-[4-(4-Tolylamino)-5-(4-tolylimino)-1,5-dihydro-2*H*-imidazol-2-ylidene]cyclohexa-2,5-dienone (7a)

Dark red solid; yield: 41%; mp > 250 °C (dec.).

IR (ATR): 1729, 3303, 3426 cm^{-1}.

^{1}H NMR (250 MHz, THF-d_8): δ = 2.41 (s, 6 H), 7.31 (d, ^3J = 8.3 Hz, 4 H), 7.39 (d, ^3J = 8.5 Hz, 1 H), 7.91 (d, ^3J = 8.3 Hz, 4 H), 8.10 (d, ^3J = 8.5 Hz, 2 H), 8.64 (d, ^3J = 8.5 Hz, 1 H).

MS (DEI): *m*/*z* (%) = 91 (22), 107 (46), 133 (15), 205 (44), 233 (100), 252 (29), 267 (12), 309 (32), 366 (10) [M]$^+$.

UV/Vis (THF): λ_{max} (log ε) = 450 (4.1), 485 (4.3), 515 nm (4.1).

CV: E_{RED}^1 = –1.01 V, E_{RED}^2 = –1.25 V.

Anal. Calcd for $C_{23}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21 Found: C, 75.03; H, 5.55; N, 15.40.

2,6-Di-*tert*-butyl-4-[4-(4-tolylamino)-5-(4-tolylimino)-1,5-dihydro-2*H*-imidazol-2-ylidene]cyclohexa-2,5-dienone (7b)
Dark red solid; yield: 37%; mp >280 °C (dec.).

IR (ATR): 1728, 3292, 3427 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 18 H), 2.36 (s, 6 H), 7.00 (s, 2 H), 7.18 (d, ^3J = 8.5 Hz, 4 H), 7.52 (d, ^3J = 8.5 Hz, 4 H), 8.43 (br s, 1 H).

^{13}C NMR (100 MHz, THF-d_8): δ = 20.9, 30.2, 34.4, 120.5, 124.2, 125.3, 129.5, 134.5, 135.7, 136.2, 143.8, 151.5, 157.1, 166.6, 182.5.

MS (DEI): *m*/*z* (%) = 91 (22), 107 (46), 133 (15), 205 (44), 233 (100), 267 (12), 339 (32), 480 (6) [M]$^+$.

UV/Vis (THF): λ_{max} (log ε) = 455 (4.1), 490 (4.2), 524 nm (4.1).

CV: E_{RED}^1 = –0.93 V, E_{RED}^2 = –1.73 V.

Anal. Calcd for $C_{31}H_{36}N_4O$: C, 77.47; H, 7.55; N, 11.66 Found: C, 77.53; H, 7.65; N, 11.75.

2,6-Di-*tert*-butyl-4-{4-[(4-*tert*-butylphenyl)amino]-5-[(4-*tert*-butylphenyl)imino]-1,5-dihydro-2*H*-imidazol-2-ylidene}cyclohexa-2,5-dienone (7c)
Dark red powder; yield: 34%; mp >300 °C (dec.).

IR (ATR): 1735, 3340, 3484 cm^{-1}.

^{1}H NMR (250 MHz, THF-d_8): δ = 1.44 (s, 18 H), 1.51 (s, 18 H), 6.99 (s, 2 H), 7.19 (d, ^3J = 8.2 Hz, 4 H), 7.56 (d, ^3J = 8.3 Hz, 4 H).

^{13}C NMR (62 MHz, THF-d_8): δ = 30.2, 31.5, 32.9, 34.5, 120.6, 124.2, 125.5, 129.7, 134.4, 135.7, 136.0, 143.8, 151.3, 157.6, 167.0, 182.4.

MS (DEI): *m*/*z* (%) = 91 (65), 106 (71), 134 (97), 159 (95), 175 (87), 233 (100), 276 (75), 293 (92), 332 (83), 352 (90), 381 (44), 507 (10), 564 (15) [M]$^+$.

UV/Vis (THF): λ_{max} (log ε) = 280 (4.3), 491 (4.1), 520 nm (4.1).

CV: E_{RED}^1 = –0.96 V, E_{RED}^2 = –1.82 V.

Anal. Calcd for $C_{37}H_{48}N_4O$: C, 78.68; H, 8.57; N, 9.92 Found: C, 78.58; H, 8.65; N, 9.90.

4-[4-(4-Tolylamino)-5-(4-tolylimino)-1,5-dihydro-2*H*-imidazol-2-ylidene]cyclohexa-2,5-dienethione (7d)
Dark red solid; yield: 23%.

IR (film): 1630, 3447 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.39 (s, 6 H), 7.31 (d, ^3J = 8.5 Hz, 4 H), 7.52 (d, ^3J = 8.0 Hz, 2 H), 7.88 (d, ^3J = 8.5 Hz, 4 H), 7.99 (d, ^3J = 8.0 Hz, 2 H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.5, 117.7, 125.3, 128.3, 129.1, 137.8, 138.4, 145.0, 163.4, 173.5, 187.6.

MS (DEI): *m*/*z* (%) = 77 (35), 91 (25), 106 (83), 131 (61), 136 (100), 243 (16), 296 (53), 369 (26), 383 (32), 384 (14) [M]$^+$.

UV/Vis (THF): λ_{max} (log ε) = 416 (3.9), 485 (4.2), 523 nm (4.1).

Anal. Calcd for $C_{23}H_{20}N_4S$: C, 71.85; H, 5.24; N, 14.57; S, 8.34 Found: C, 71.78; H, 5.18; N, 14.60; S, 8.42.

2,6-Di-*tert*-butyl-4-(4-{[4-(dimethylamino)phenyl]amino}-5-{[4-(dimethylamino)phenyl]imino}-1,5-dihydro-2*H*-imidazol-2-ylidene)cyclohexa-2,5-dienone (7e)
Purple solid; yield: 20%.

IR (ATR): 1730, 3621 cm^{-1}.

^{1}H NMR (250 MHz, THF-d_8): δ = 1.44 (s, 18 H), 3.00 (s, 12 H), 6.79 (d, ^3J = 8.5 Hz, 4 H), 8.09 (d, ^3J = 8.5 Hz, 4 H), 8.15 (s, 2 H).

MS (DEI): *m*/*z* (%) = 104 (41), 136 (58), 145 (35), 166 (33), 205 (100), 233 (83), 338 (6), 368 (5), 469 (25), 538 (28) [M]$^+$, 539 (41) [M + H]$^+$.

UV/Vis (THF): λ_{max} (log ε) = 266 (4.2), 312 (4.1), 484 (4.1), 569 nm (4.2).

Anal. Calcd for $C_{33}H_{42}N_6O$: C, 73.57; H, 7.86; N, 15.60; Found: C, 73.66; H, 7.78; N, 15.72.

Reduction of Derivatives 7; General Procedure
A mixture of **7** (1.0 mmol), THF (50 mL) and 0.06 M $Na_2S_2O_4$ soln (10 mL) was stirred at r.t. for 15 min. During the reduction the color of the soln changed from deeply red to yellow. The solvent was removed in vacuo. Leuco forms **9** were obtained as yellowish solids, which immediately reoxidize when exposed to air. Therefore, no accurate MS and NMR spectra could be obtained.

2,6-Di-*tert*-butyl-4-[4,5-bis(4-tolylamino)-1*H*-imidazol-2-yl]phenol (9b)
Yellow solid; yield: 100%.

UV/Vis (THF): λ_{max} (log ε) = 405 nm (4.1).

Fluorescence (THF, 407 nm): $\lambda_{max,em}$ = 473 nm.

2,6-Di-*tert*-butyl-4-{4,5-bis[(4-*tert*-butylphenyl)amino]-1*H*-imidazol-2-yl}phenol (9c)
Yellow solid; yield: 100%.

UV/Vis (THF): λ_{max} (log ε) = 408 nm (4.1).

Fluorescence (THF, 409 nm): $\lambda_{max,em}$ = 470 nm.

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References

(1) Matschke, M.; Beckert, R. *Molecules* **2007**, *12*, 723.
(2) Blumhoff, J.; Beckert, R.; Walther, D.; Rau, S.; Rudolph, M.; Görls, H.; Plass, W. *Eur. J. Inorg. Chem.* **2007**, *3*, 481.
(3) Matschke, M.; Käpplinger, C.; Weiß, D.; Beckert, R. *Tetrahedron Lett.* **2005**, *46*, 8249.
(4) Matschke, M.; Käpplinger, C.; Weiß, D.; Albrecht, S.; Distler, W.; Beckert, R. DE 102,005,034,129, **2007**.
(5) Büchel, K. H.; Erdmann, H. *Chem. Ber.* **1976**, *109*, 1638.
(6) Büchel, K. H.; Erdmann, H. *Chem. Ber.* **1977**, *110*, 3226.
(7) Fabian, J.; Beckert, R.; Atzrodt, J. *J. Prakt. Chem./Chem.-Ztg.* **1997**, *339*, 735.
(8) Atzrodt, J.; Brandenburg, J.; Käpplinger, C.; Beckert, R.; Günther, W.; Görls, H.; Fabian, J. *J. Prakt. Chem./Chem.-Ztg.* **1997**, *339*, 729.
(9) Müller, D.; Beckert, R.; Görls, H. *Synthesis* **2001**, 601.
(10) Perry, C.; Parveen, Z. *J. Chem. Soc., Perkin Trans. 2* **2001**, 512.
(11) Bargellini, G. *Gazz. Chim. Ital.* **1904**, *34/II*, 455.
(12) Hellwinkel, D.; Lenz, R.; Lammerzahl, F. *Tetrahedron* **1983**, *39*, 2073.

(13) Zee-Cheng, R.; Cheng, C. *J. Med. Chem.* **1985**, *28*, 1216.
(14) Bryce-Smith, D.; Gilbert, A.; McColl, I. S.; Drew, M. G.; Yianni, P. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1147.
(15) Mullican, M.; Wilson, M.; Connor, D.; Kostlan, C.; Schrier, D.; Dyer, R. *J. Med. Chem.* **1993**, *36*, 1090.
(16) Bis(alkylsulfanyl)quinomethides: Gompper, R.; Kutter, E. *Chem. Ber.* **1965**, *98*, 1374.
(17) Gebauer, T.; Beckert, R.; Weiß, D.; Knop, K.; Käpplinger, C.; Görls, H. *Chem. Commun.* **2004**, 1860.
(18) Käpplinger, C.; Beckert, R.; Günther, W.; Görls, H. *Liebigs Ann./Recl.* **1997**, 617.
(19) Matschke, M.; Käpplinger, C.; Beckert, R. *Tetrahedron* **2006**, *62*, 8586.
(20) Neidlein, R.; Hartz, G. *Helv. Chim. Acta* **1986**, *69*, 315.
(21) Grossmann, N.; Wehner, V.; Weise, A.; Winning, B.; Fanghaenel, E. *J. Prakt. Chem.* **1988**, *330*, 204.
(22) Xie, C.; Lahti, P. M. *Tetrahedron Lett.* **1999**, *40*, 4305.