



4*H*-Imidazoles as functional dyes: synthesis of bichromophores and extension of the merocyanine system

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ABSTRACT

A series of bichromophores consisting of a 'classical' chromophore and 4*H*-imidazoles were synthesized starting from appropriate cyano and carboxy functionalized systems. In their UV–vis spectra, an additive absorption of both chromophores was detected making them wide range-absorbing dyes. In addition, new properties as redox activity, pH-switchability and metal-chelating substructures are newly introduced into the molecules. In order to achieve more bathochromic absorbing systems, the chromophore of 4*H*-imidazoles was extended. The 4*H*-imidazo-[1,2-*a*]-pyridines, which are easily accessible by cyclization of 2-aminopyridines with bis-imidoylchlorides, show long wavelength absorptions up to 616 nm. Their reduction reversibly yields yellow, blue fluorescent 1-azaindolizines. In contrast to leuco-forms of 4*H*-imidazoles, these reduction products show a high stability towards oxygen and could only be reoxidized to their starting materials by oxidation agents, such as DDQ.

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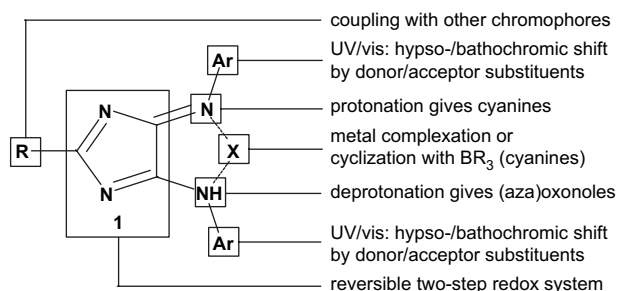
1. Introduction

The combination of two or more chromophores is of recent interest in material sciences, e.g., for the synthesis of novel antenna systems. Such antenna systems are widely used by nature to solve the problem of light harvesting efficiency in the photosynthetic processes. Antennas are well-organized multicomponent systems in which several chromophoric subspecies absorb the sunlight and channel the excitation energy to an acceptor part. In addition to the solar energy conversion, there is a strong need for antenna systems, for example, in signal amplification in luminescence sensors, for light-driven reactions/catalyses and in sensitization of photovoltaics. All these applications are based on tailor-made multi-chromophores, which are arranged in supramolecular arrays suitably organized in the dimensions of time, energy and space.

Typical chromophores, which were often employed are porphyrins, the main chromophores of natural photosynthesis. Further systems used as part of a multi-chromophoric assembly are: bodypys,¹ peryleneimides,² coumarines,³ eosine⁴ and others.

In the last decade, in our group the 4*H*-imidazoles **1** were developed as a new class of functional dyes: dependent on their substituents, they show absorptions in a wide range of the visible spectrum,⁵ are pH-switchable,⁶ reversible two-electron-redoxsystems⁷ and efficient chelating ligands for metals (Scheme 1).⁸ Our

aim was to connect classic chromophores with 4*H*-imidazoles and to study the properties of the resulting bichromophores.



Scheme 1. 4*H*-Imidazoles—cyclic merocyanines and functional dyes.

2. Results and discussion

In the framework of this study, different chromophores were involved in order to obtain general information concerning the new bichromophores. A comparison with already existing derivatives, which contain conjugated⁹ and non-conjugated¹⁰ structural elements, should clarify the question if an additive behaviour⁹ of the subchromophores exists.

The direct coupling of the chromophores was ruled out, due to the fact that 4*H*-imidazoles proved to be inactive in all attempts using metal-catalyzed cross-coupling methods. Therefore, another synthetic entry was chosen: cycloacylation reactions of amidines **3**

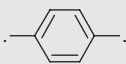
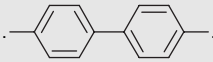
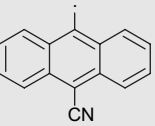
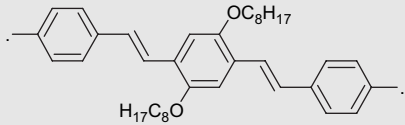
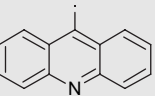
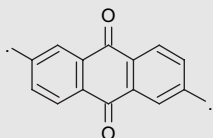
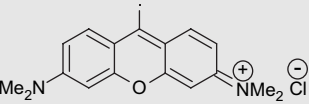
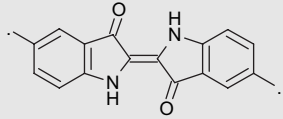
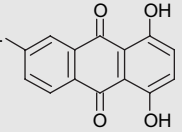
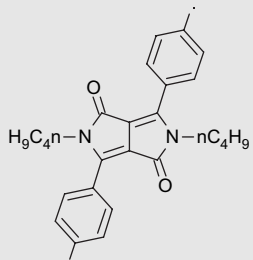
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lated in yields up to 55% as dark red to deep purple, mostly crystalline solids. Compared with 2-arylsubstituted 4*H*-imidazoles, the ring-fused derivatives **9**, which also can be described as betaines of 1-aza-2*H*-indolizine²⁵ show some differences.

Table 1
Absorption properties of synthesized chromophores and bichromophores derived from 4*H*-imidazoles



R	Ar	λ_{max} in nm (log ϵ)	X	Ar	λ_{max} in nm (log ϵ)
<i>Aliphatic substituents</i>			<i>Conjugative bridging-units</i>		
	Ar ²	461 (4.2) ^b		Ar ²	479 (4.2), 533 (4.2) ^a
<i>Aromatic substituents</i>					
	Ar ¹	488 (4.2) ^a		Ar ¹	511 (4.1), 545 (4.1) ^a
	Ar ¹	496 (4.2) ^b		Ar ¹	497 (4.1), 527 (4.0) ^a
	Ar ¹	480 (4.3), 520 (4.2) ^a		Ar ¹	504 (4.6), 540 (4.4) ^a
<i>Substitution by longwave absorbing chromophores</i>					
 8a	Ar ¹	481 (4.3) ^b	 8d	Ar ¹	513 (4.4), 544 (4.2) ^a
 8c	Ar ¹	508 (4.0), 595 (3.5) ^c	 8g	Ar ¹	523 (4.2), 622 (3.6) ^a
 8e	Ar ¹	512 (3.9), 615 (3.7) ^a	 8f	Ar ¹	524 (4.3) ^a

$$\text{Ar}^1=4\text{-CH}_3\text{-C}_6\text{H}_4\text{-}, \text{Ar}_2=4\text{-}t\text{-C}_4\text{H}_9\text{-C}_6\text{H}_4\text{-}.$$

^a The UV-vis spectra were measured in THF.

^b The UV-vis spectra were measured in CHCl₃.

^c The UV-vis spectra were measured in MeOH.

The ^1H NMR spectra of the parent compounds **1** show single signal sets caused by a very fast prototropism between peripheral arylamino/imino-groups, which reflects a high symmetry of the molecules. In contrast, the NMR spectra of derivatives **9** show double signal sets. Both mesomeric forms (**9'** and **9''**) suggest

negative charges at the imino-nitrogen atoms. However, all attempts to protonate this nitrogen as well as to perform simple alkylation or acylation reactions failed. Treatment of **9a** with strong alkylating agents such as trialkyloxonium salts led to the formation of extremely unstable pyridinium salts, which fastly

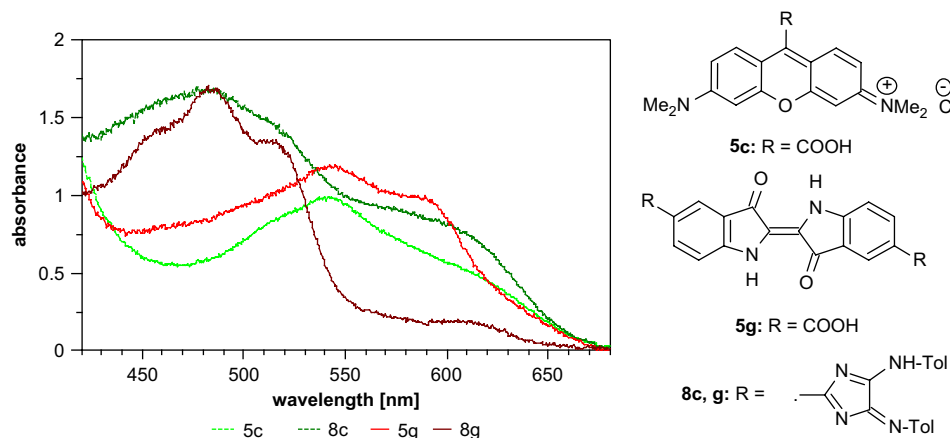
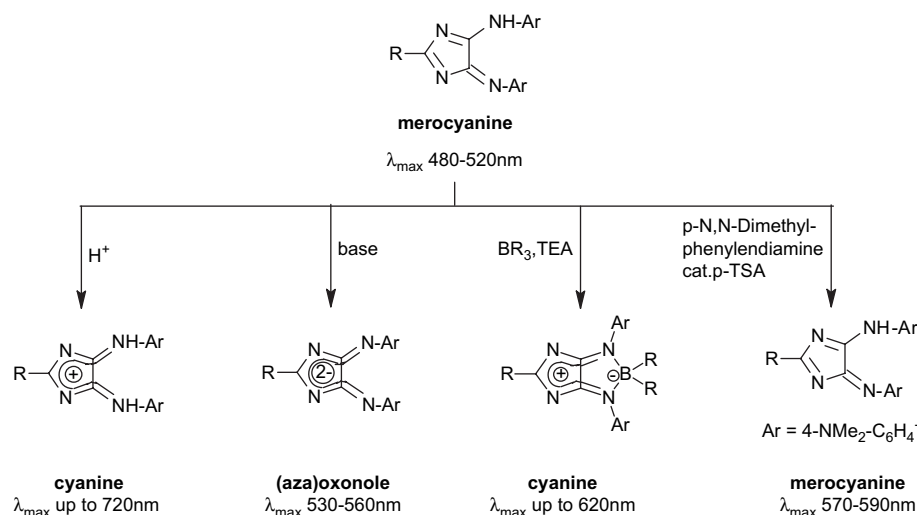


Figure 1. UV-vis spectra of integrated chromophores **5c, g** and obtained bichromophores **8c, g**.



Scheme 3. Derivatization reactions of 4*H*-imidazoles.

Table 2

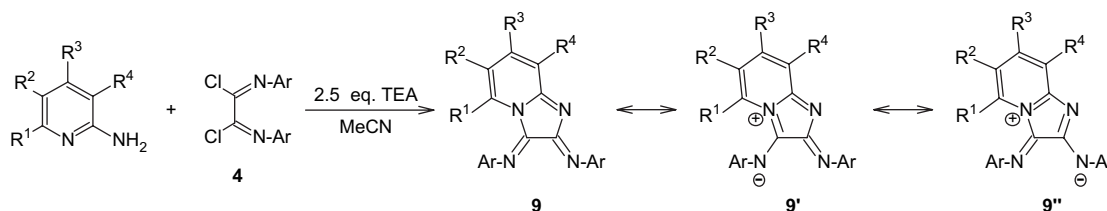
Longest wavelength absorptions of synthesized 4*H*-imidazo-[1,2-*a*]-pyridines **9**

No.	R	Ar	Yield (%)	$\lambda_{\max}$ in nm (log ϵ) [CHCl ₃]
9a	R ¹ –R ⁴ =H	4-CH ₃ –C ₆ H ₄ –	41	586 (3.9)
9b	R ¹ –R ⁴ =H	4- <i>n</i> -C ₄ H ₉ –C ₆ H ₄ –	38	585 (3.9)
9c	R ¹ –R ⁴ =H	2,6- <i>i</i> -C ₃ H ₇ –C ₆ H ₃ –	22	531 (3.9)
9d	R ¹ –R ⁴ =H	2,4,6-CH ₃ –C ₆ H ₂ –	21	556 (3.9)
9e	R ¹ –R ⁴ =H	4-CH ₃ –C ₆ H ₄ –	35	616 (3.9)
9f	R ² =NO ₂ –	4-CH ₃ –C ₆ H ₄ –	27	534 (3.8)
9g	R ³ , R ⁴ =1,2-C ₆ H ₄ –	4-CH ₃ –C ₆ H ₄ –	55	534 (3.9)

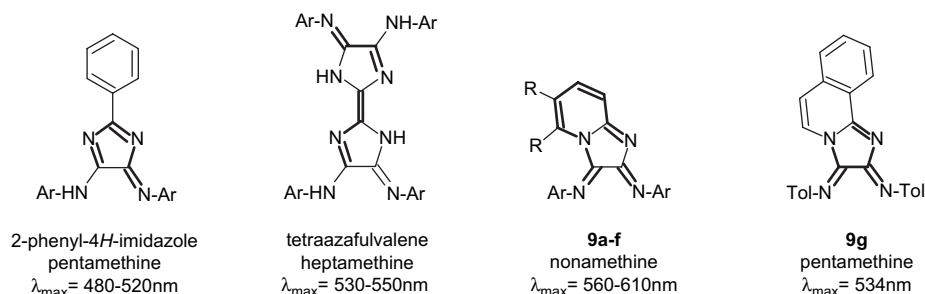
decomposed to tolylisocyanide and mixtures of unseparable compounds. This very low stability might be caused by the far reaching similarity to other pyridinium salts, known as acyl-transfer-reagents.²⁶

With respect to 4*H*-imidazoles **1**, the most outstanding property of derivatives **9a–e** is their 80–100 nm bathochromic shifted absorption, which results in a deep purple colour of their solutions. The integration of the pyridine ring causes extension of the chromophore of **1** by four methine units forming a new non-amethine–merocyanine. The strong electron-accepting character of the nitro-group in derivative **9f** resulted in a hypsochromic shift of the long wavelength absorption in its UV-vis-spectrum as well as a small hypochromic effect (Table 2).

The integration of additional condensed ring-systems does not expand the chromophoric system. As demonstrated with the 4*H*-imidazo-[1,2-*a*]-isochinoline **9g**, the characteristic chromophore of 4*H*-imidazoles is predominant. The chromophoric system of tetraazafulvalenes, which were also synthesized in our research group,²⁷ is based on two crossed diazaheptamethine–



Scheme 4. Synthesis of 4*H*-imidazo-[1,2-*a*]-pyridines **9**.

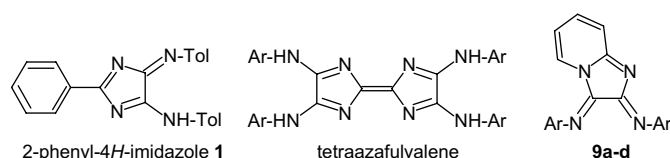


Scheme 5. Diazapolymethine-merocyanines based on cycloamidines.

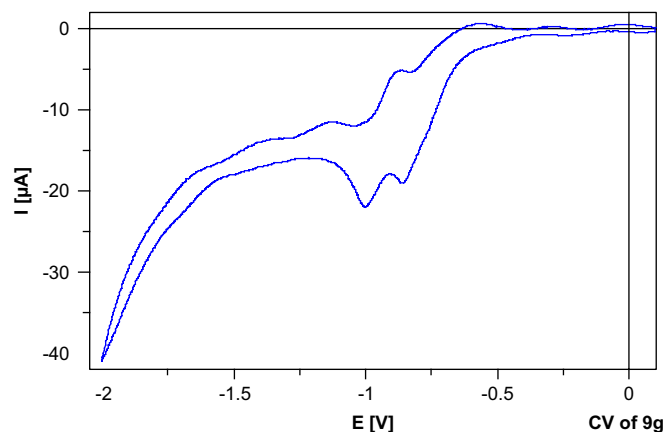
merocyanines. Their absorptions, which are located in the range of 530–550 nm fit well into the system of merocyanines (Scheme 5).

In comparison to acyclic merocyanines of type $(\text{CH}_3)_2\text{N}-(\text{CH}=\text{CH})_{n-1}-\text{CH}=\text{O}$,²⁸ which possess the same number of methine units, the cyclic diazapolymethine-merocyanines show a bathochromic shift of about 120 nm.

Similar to their parent derivatives **1**, the 4H-imidazo-[1,2-a]-pyridines **9** show quasi-reversibility of the reduction, evidenced chemically as well as electrochemically. The comparison of the



No.	chromophore	$E_{\text{RED}}^1, E_{\text{RED}}^2$	K_{SEM}
1	pentamethine	-1.26 V, -1.39 V	$1.6 \cdot 10^2$
9g	pentamethine	-0.83 V, -0.98 V	$4.1 \cdot 10^2$
TAF	heptamethine	-0.69 V, -0.83 V	$1.7 \cdot 10^2$
9a	nonamethine	-0.80 V, -0.95 V	$4.1 \cdot 10^2$
9b	nonamethine	-0.81 V, -0.95 V	$2.4 \cdot 10^2$
9c	nonamethine	-1.01 V, -1.12 V	$7.4 \cdot 10^1$
9d	nonamethine	-0.88 V, -1.03 V	$4.1 \cdot 10^2$

Figure 2. Electrochemical data of different diazapolymethine-merocyanine chromophores and cyclic voltammogram of **9g**.

semiquinone formation constants K_{SEM} of the three azamerocyanines (4H-imidazoles, tetraazafulvalenes, 4H-imidazo-[1,2-a]-pyridines) indicates a low thermodynamic stability of the intermediates (radical anion=SEM form), which are not influenced by the length of the conjugated system (Fig. 2).



No.	R	$\lambda_{\max}$ (log ϵ)	$\lambda_{\max, \text{em}}$ ($\lambda_{\max, \text{exc}}$)
10a	$\text{R}^1\text{-R}^4 = \text{H}$	375 nm (3.9)	470 nm (382 nm)
10b	$\text{R}^1\text{-R}^4 = \text{H}$	391 nm (3.9)	474 nm (392 nm)
10c	$\text{R}^1\text{-R}^4 = \text{H}$	376 nm (3.9)	476 nm (375 nm)
10d	$\text{R}^1\text{-R}^4 = \text{H}$	450 nm (3.9)	532 nm (454 nm)
10e	$\text{R}^1 = \text{CH}_3^-$	475 nm (3.9)	554 nm (479 nm)
10f	$\text{R}^2 = \text{NO}_2^-$	470 nm (3.8)	475 nm (470 nm)
10g	$\text{R}^3, \text{R}^4 = 1,2\text{-C}_6\text{H}_4^-$	440 nm (3.9)	474 nm (438 nm)

Scheme 6. Reduction of **9** and absorption/emission data of the 2,3-bis-(arylamino)-1-azaindolizines **10**.

The reduction of derivatives of type **9** with aqueous sodium dithionite yields yellow, greenish-blue fluorescent products (Scheme 6). Elemental analysis, MS and NMR data confirm the structure of 1-azaindolizines **10**. However, in contrast to the reduction products of 4H-imidazoles, these leuco-forms were not reoxidized when exposed to air. Even standing at room temperature within 1–2 days, they decompose leading to complex mixtures consisting mainly of 2-aminopyridine and the corresponding arylamine ArNH_2 (TLC). Reoxidation only takes place in the presence of strong oxidizing agents, e.g., DDQ to give starting material **9**. All attempts to modify the leuco-forms by alkylation or acylation reactions failed.

3. Conclusions

The synthesis of a number of bichromophores starting from classical chromophores and one or two 4H-imidazoles is reported. All synthesized derivatives were fully characterized by MS, NMR and IR. Their UV-vis spectra show an overlap of the chromophores resulting in wide range-absorbing systems. Due to the integration of 4H-imidazoles in bi-/multichromophores some useful functionalities were generated:

- redox activity (derivates **8** and **9** can be regarded as multi-step redox systems)
- all systems are pH-switchable
- the peripheric amino/imino substructures of 4H-imidazoles offer good requirements for the formation of metal chelate complexes.

The concept of cycloamidines could be expanded to non-amethine–merocyanines. They can easily be obtained by cyclization of 2-aminopyridines with bis-imidoylchlorides. The obtained 4*H*-imidazo-[1,2-*a*]-pyridines **9** show long wavelength absorptions up to 616 nm in their UV–vis spectra. Comparable to 4*H*-imidazoles, they are two-step redox systems indicated by electrochemical measurements, which showed the reversibility of their reduction. However, the products of chemical reductions—1-azaindolizines **10**—are yellow, blue fluorescent compounds, which proved to be stable towards oxygen. On treatment with oxidizing agents such as DDQ, their reoxidation could be realized yielding derivatives **9**. In summary, tailor-made 4*H*-imidazoles are of interest for applications in functional dyes.

4. Experimental

4.1. General

All reactions were monitored by TLC, carried out on 0.25 mm Merck silica gel plates (60 F₂₅₄) using UV light. ¹H and ¹³C 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 mercury or platinum electrodes and tetrabutylammoniumhexafluorophosphate as conductive salt.

For synthesis and analytic data of 4*H*-imidazoles with aliphatic^{10,11} and aromatic substituents including derivatives **8a**, **8h** and **8i**,^{10,11,29} as well as bis-4*H*-imidazoles with conjugative bridging-units⁹ (Table 1), see the given literatures. Bichromophores **8c–g** were synthesized according to literature procedures.¹¹

4.1.1. 9-[5-*p*-Tolylamino-4-(*p*-tolylimino)-4*H*-imidazol-2-yl]-3,6-bis-(dimethylamino)-xanthyliumchloride (**8c**)

Yield: 12%, brown solid, mp>250 °C (decomp.); ¹H NMR (250 MHz, CDCl₃): δ 2.28 (s, 12H), 2.35 (s, 6H), 7.15–7.25 (m, 8H), 7.36 (d, ³J=8.3 Hz, 4H), 7.88 (d, ³J=8.2 Hz, 2H); ¹³C NMR (62 MHz, CDCl₃): δ 21.1, 34.2, 100.0, 115.5, 125.4, 128.3, 129.6, 130.7, 131.6, 132.9, 134.0, 135.8, 148.2, 151.5, 162.2, 170.3; MS (DEI): *m/z* (%): 547 (M)⁺ (17), 546 (33), 396 (43), 268 (83), 220 (100), 205 (90), 177 (29), 145 (35), 133 (46), 105 (35), 91 (43), 57 (69); IR (film): 3640, 1513, 1434 cm^{−1}; UV–vis (MeOH) λ_{max} (log ε): 457 (4.1), 480 (4.2), 508 (4.0), 595 (3.5) nm. Fluorescence (MeOH, 480 nm) λ_{max,em}: 577 nm, λ_{max,exc}: 380 nm, λ_{max,em}: 412 nm.

4.1.2. 5,5'-Bis-(*p*-tolylamino)-4,4'-bis-(*p*-tolylimino)-4*H*,4'*H*-2,2'-(2,6-anthraquinone)-biimidazole (**8d**)

Yield: 10%, metallic red shining solid, mp>250 °C (decomp.); NMR: no valuable spectra were obtained caused by too poor solubility; MS (DEI): *m/z* (%): 758 (M)⁺ (8), 653 (10), 506 (29), 492 (33), 370 (26), 363 (44), 248 (40), 234 (35), 106 (100); IR (film): 3345, 1676 cm^{−1}; UV–vis (THF) λ_{max} (log ε): 405 (4.2), 429 (4.2), 481 (4.2), 513 (4.4), 544 (4.2) nm; CV: E_{RED}¹=−0.60 V, E_{RED}²=−1.10 V.

4.1.3. 2-[5-*p*-Tolylamino-4-(*p*-tolylimino)-4*H*-imidazol-2-yl]-5,8-dihydroxy-9,10-anthraquinone (**8e**)

Yield: 8%, red-brown solid, mp>300 °C (decomp.); ¹H NMR (250 MHz, CDCl₃): δ 2.28 (s, 6H), 6.99 (s, 1H), 7.07 (d, ³J=8.5 Hz, 4H), 7.17 (d, ³J=8.5 Hz, 1H), 7.32 (m, 6H), 7.55 (m, 2H); ¹³C NMR (62 MHz, CDCl₃): δ 21.2, 123.1, 123.2, 125.5, 126.5, 128.3, 130.1, 130.2, 130.6, 130.7, 135.8, 139.5, 151.5, 155.3, 167.8, 176.4, 186.0; MS (DEI): *m/z* (%): 515 (M+1)⁺ (23), 408 (11), 337 (6), 279 (25), 203 (18), 173 (45), 131 (83), 91 (100), 77 (74); IR (ATR): 3642, 3363 (br), 1743 cm^{−1}; UV–vis

(THF) λ_{max} (log ε): 409 (4.1), 512 (3.9), 615 (3.7) nm; Fluorescence (THF, 480 nm) λ_{max,em}: 605 nm.

4.1.4. 5,5'-Bis-(*p*-tolylamino)-4,4'-bis-(*p*-tolylimino)-4*H*,4'*H*-2,2'-(5,5'-indigo)-biimidazole (**8g**)

Yield: 10%, dark red powder, mp>300 °C (decomp.); ¹H NMR (250 MHz, CDCl₃): δ 2.28 (s, 12H), 6.99 (m, 10H), 7.08 (d, ³J=8.3 Hz, 2H), 7.18 (d, ³J=8.3 Hz, 2H), 7.28 (d, ³J=8.3 Hz, 8H), 7.95 (s, 2H); ¹³C NMR (62 MHz, CDCl₃): δ 22.7, 117.8, 119.8, 123.8, 125.5, 128.2, 129.6, 129.7, 129.8, 130.0, 135.8, 151.5, 163.3, 173.2, 191.4; MS (FAB in nba): *m/z* (%): 811 (M)⁺ (9), 721 (12), 578 (14), 505 (18), 461 (23), 327 (39), 281 (45), 265 (51), 219 (89), 207 (100); IR (film): 3648, 3300, 1738 cm^{−1}; UV–vis (THF) λ_{max} (log ε): 408 (3.9), 473 (4.2), 503 (4.3), 523 (4.2), 622 (3.6) nm.

4.2. General procedure for the synthesis of 4*H*-imidazo-[1,2-*a*]-pyridines (**9**)

The corresponding aminopyridine (2.0 mmol) or 1-aminoisoquinoline (288 mg, 2.0 mmol) was added to a solution of 2.0 mmol oxalic acid bis-imidoylchloride in 20 ml of acetonitrile. After addition of 0.7 ml (5.0 mmol) triethylamine, the reaction mixture was heated under reflux for about 4–5 h. The deep red-violet solution was cooled to rt, evaporated to dryness and the product was isolated by column chromatography (SiO₂, toluene/acetone 100:1). The 4*H*-imidazo-[1,2-*a*]-pyridines **9** were obtained as dark red-violet crystalline solids after removing the solvents.

4.2.1. 2,3-Bis-(4-tolylimino)-2*H*-imidazo-[1,2-*a*]-pyridine (**9a**)

Yield: 267 mg (41%), golden shining crystals, mp 139–140 °C; ¹H NMR (250 MHz, CDCl₃): δ 2.30 (s, 3H), 2.37 (s, 3H), 6.40 (t, ³J=6.5 Hz, 1H), 6.91 (d, ³J=9.2 Hz, 1H), 7.10 (d, ³J=8.0 Hz, 2H), 7.17 (d, ³J=8.0 Hz, 2H), 7.35 (d, ³J=8.0 Hz, 2H), 7.43 (d, ³J=8.0 Hz, 2H), 7.55 (t, ³J=6.5 Hz, 1H), 8.01 (d, ³J=6.8 Hz, 1H); ¹³C NMR (62 MHz, CDCl₃): δ 21.2, 30.9, 109.2, 117.4, 119.8, 122.6, 125.5, 127.6, 128.8, 129.1, 129.8, 135.5, 135.9, 141.1, 142.5, 145.4, 145.6; MS (DEI): *m/z* (%): 328 (M+2)⁺ (82), 311 (43), 235 (21), 222 (33), 209 (51), 183 (29), 131 (23), 116 (55), 106 (94), 91 (100), 78 (100); IR (ATR): 1649, 1608, 1568, 1479 cm^{−1}; UV–vis (THF) λ_{max} (log ε): 248 (4.4), 306 (4.2), 505 (4.0), 543 (4.1), 586 (3.9) nm; CV: E_{RED}¹=−0.80 V, E_{RED}²=−0.95 V. Anal. Calcd for C₂₁H₁₈N₄: C, 77.28; H, 5.55; N, 17.17. Found: C, 77.03; H, 5.50; N, 17.47.

4.2.2. 2,3-Bis-(4-*n*-butylphenylimino)-2*H*-imidazo-[1,2-*a*]-pyridine (**9b**)

Yield: 312 mg (38%), black violet solid; ¹H NMR (400 MHz, CDCl₃): δ 0.96 (s, 3H), 0.99 (s, 3H), 1.35–1.48 (m, 4H), 1.58–1.75 (m, 4H), 2.62 (t, ³J=8.0 Hz, 2H), 2.69 (t, ³J=7.2 Hz, 2H), 6.38 (t, ³J=6.4 Hz, 1H), 6.72 (d, ³J=6.4 Hz, 1H), 7.38 (t, ³J=6.4 Hz, 1H), 7.47 (d, ³J=8.4 Hz, 2H), 7.50 (d, ³J=8.4 Hz, 2H), 7.60 (d, ³J=6.8 Hz, 2H), 7.63 (d, ³J=7.6 Hz, 2H), 8.00 (d, ³J=6.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.0, 21.5, 22.3, 33.7, 35.2, 109.3, 115.8, 117.4, 119.9, 122.6, 124.5, 125.3, 125.9, 127.4, 128.1, 128.3, 128.6, 128.9, 129.2, 129.7, 130.4, 130.7, 131.6, 145.4, 145.8, 149.3, 151.3, 157.5, 162.8; MS (DEI): *m/z* (%): 411 (M+1)⁺ (51), 355 (39), 309 (47), 259 (71), 228 (74), 208 (65), 166 (69), 149 (73), 106 (74), 91 (100), 57 (27); IR (ATR): 1654, 1605, 1530, 1489 cm^{−1}; UV–vis (CHCl₃) λ_{max} (log ε): 406 (3.9), 498 (3.9), 535 (4.0), 585 (3.9) nm; CV: E_{RED}¹=−0.81 V, E_{RED}²=−0.95 V. Anal. Calcd for C₂₇H₃₀N₄: C, 78.99; H, 7.36; N, 13.65. Found: C, 78.91; H, 7.50; N, 13.59.

4.2.3. 2,3-Bis-(2,6-diisopropylphenylimino)-2*H*-imidazo-[1,2-*a*]-pyridine (**9c**)

Yield: 205 mg (22%), black violet solid, mp 182–184 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.19 (d, ³J=6.8 Hz, 12H), 1.25 (d, ³J=6.8 Hz, 12H),

2.8–3.0 (m, 4H), 6.85 (t, $^3J=6.5$ Hz, 1H), 6.87 (t, $^3J=6.5$ Hz, 1H), 7.06 (d, $^3J=4.8$ Hz, 1H), 7.15–7.20 (m, 3H), 7.23–7.30 (m, 3H), 7.34–7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 22.0, 22.8, 23.4, 28.3, 28.9, 109.4, 117.9, 122.6, 122.7, 124.1, 125.3, 128.2, 129.0, 134.9, 136.8, 137.9, 141.7, 145.4, 163.5; MS (DEI): m/z (%): 466 (M^+) (31), 451 (93), 423 (100), 357 (39), 278 (95), 264 (91), 238 (89), 220 (25), 186 (87), 170 (43), 91 (35), 43 (27); IR (ATR): 1658, 1604, 1504, 1463 cm^{-1} ; UV–vis (CHCl_3) λ_{max} (log ϵ): 270 (4.2), 464 (3.9), 492 (4.0), 531 (3.9) nm; CV: $E_{\text{RED}}^1=-1.01$ V, $E_{\text{RED}}^2=-1.12$ V. Anal. Calcd for $\text{C}_{31}\text{H}_{38}\text{N}_4$: C, 79.78; H, 8.21; N, 12.01. Found: C, 79.65; H, 8.20; N, 12.15.

4.2.4. 2,3-Bis-(2,4,6-trimethylphenylimino)-2H-imidazo-[1,2-a]-pyridine (**9d**)

Yield: 160 mg (21%), black, metallic shining crystals, mp 101–103 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.22 (s, 3H), 2.29 (s, 6H), 2.37 (s, 3H), 2.69 (s, 6H), 6.48 (d, $^3J=8.4$ Hz, 1H), 7.10 (s, 2H), 7.1–7.2 (m, 2H), 7.26 (s, 2H), 7.97 (d, $^3J=8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 18.5, 18.9, 20.7, 20.9, 21.4, 109.0, 113.7, 115.8, 125.3, 128.2, 128.6, 129.0, 129.5, 132.3, 133.0, 135.4, 138.0, 140.4, 140.7, 143.3, 145.3, 147.1, 156.8, 158.3, 162.2; MS (DEI): m/z (%): 381 ($\text{M}-1$)⁺ (4), 234 (19), 228 (1), 206 (17), 161 (55), 91 (43), 77 (31), 67 (100), 58 (40), 39 (66), 28 (78); IR (ATR): 1651, 1599, 1499, 1476 cm^{-1} ; UV–vis (CHCl_3) λ_{max} (log ϵ): 388 (3.7), 398 (3.7), 481 (3.9), 517 (4.0), 556 (3.9) nm; CV: $E_{\text{RED}}^1=-0.88$ V, $E_{\text{RED}}^2=-1.03$ V. Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{N}_4$: C, 78.50; H, 6.85; N, 14.65. Found: C, 78.45; H, 6.93; N, 14.62.

4.2.5. 2,3-Bis-(4-tolylimino)-2H-imidazo-[1,2-a]-5-methylpyridine (**9e**)

Yield: 238 mg (35%), black violet solid; ^1H NMR (400 MHz, CDCl_3): δ 2.17 (s, 3H), 2.25 (s, 3H), 2.35 (s, 3H), 6.65 (d, $^3J=9.0$ Hz, 2H), 6.83 (d, $^3J=7.0$ Hz, 1H), 6.87 (d, $^3J=7.0$ Hz, 1H), 7.05 (t, $^3J=8.5$ Hz, 1H), 7.20 (d, $^3J=8.2$ Hz, 2H), 7.65 (d, $^3J=8.2$ Hz, 2H), 7.74 (d, $^3J=8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.2, 30.9, 110.3, 116.0, 119.9, 120.2, 125.3, 128.5, 129.3, 129.4, 129.7, 130.4, 133.0, 135.7, 139.8, 141.3, 141.7, 142.6, 146.1; MS (DEI): m/z (%): 340 (M^+) (2), 339 ($\text{M}-1$)⁺ (4), 338 ($\text{M}-2$)⁺ (12), 206 (16), 149 (21), 133 (41), 106 (100), 77 (23); IR (ATR): 1597, 1575, 1457 cm^{-1} ; UV–vis (CHCl_3) λ_{max} (log ϵ): 539 (3.9), 575 (4.0), 616 (3.9) nm. Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_4$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.49; H, 5.91; N, 16.60.

4.2.6. 2,3-Bis-(4-tolylimino)-2H-imidazo-[1,2-a]-6-nitropyridine (**9f**)

Yield: 200 mg (27%), dark red solid; ^1H NMR (250 MHz, CDCl_3): δ 2.28 (s, 3H), 2.41 (s, 3H), 6.83 (d, $^3J=8.0$ Hz, 2H), 6.9–7.3 (m, 7H), 7.54 (d, $^3J=8.5$ Hz, 1H), 7.91 (d, $^3J=8.3$ Hz, 1H); ^{13}C NMR (62 MHz, CDCl_3): δ 20.9, 21.3, 107.3, 117.5, 120.3, 120.9, 129.3, 129.5, 129.9, 130.6, 132.4, 134.7, 136.6, 146.7, 147.3, 154.9, 160.7; MS (DEI): m/z (%): 371 (M^+) (2), 370 ($\text{M}-1$)⁺ (4), 324 (26), 290 (98), 205 (93), 106 (71), 91 (100), 72 (67); IR (ATR): 1638, 1595, 1558, 1505, 1291 cm^{-1} ; UV–vis (CHCl_3) λ_{max} (log ϵ): 463 (3.7), 494 (3.9), 534 (3.8) nm. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_5\text{O}_2$: C, 67.91; H, 4.61; N, 18.86. Found: C, 67.85; H, 4.54; N, 18.90.

4.2.7. 2,3-Bis-(4-tolylimino)-2H-imidazo-[1,2-a]-isoquinoline (**9g**)

Yield: 410 mg (55%), dark red solid, mp >160 °C (decomp.); ^1H NMR (250 MHz, CDCl_3): δ 2.38 (s, 3H), 2.39 (s, 3H), 6.64 (d, $^3J=7.2$ Hz, 1H), 7.15–7.25 (m, 3H), 7.29 (t, $^3J=7.2$ Hz, 1H), 7.39 (d, $^3J=8.0$ Hz, 2H), 7.55 (d, $^3J=8.0$ Hz, 2H), 7.58 (d, $^3J=8.0$ Hz, 2H), 7.71 (t, $^3J=6.8$ Hz, 1H), 7.79 (d, $^3J=7.2$ Hz, 1H), 8.48 (d, $^3J=7.6$ Hz, 1H); ^{13}C NMR (62 MHz, CDCl_3): δ 21.0, 21.5, 109.3, 121.4, 122.1, 125.3, 126.7, 127.1, 127.2, 128.1, 128.2, 129.1, 129.3, 134.0, 136.2, 143.4, 145.2, 145.9, 151.3, 157.5, 162.6; MS (DEI): m/z (%): 376 (M^+) (11), 375 (21), 361 (20), 285 (17), 268 (14), 258 (31), 128 (60), 106 (54), 91 (100); IR

(ATR): 1643, 1612, 1583, 1551, 1494, 1467 cm^{-1} ; UV–vis (CHCl_3) λ_{max} (log ϵ): 272 (4.4), 457 (3.9), 502 (4.0), 534 (3.9) nm; CV: $E_{\text{RED}}^1=-0.83$ V, $E_{\text{RED}}^2=-0.98$ V. Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{N}_4$: C, 79.76; H, 5.35; N, 14.88. Found: C, 79.69; H, 5.25; N, 14.96.

4.3. Reduction of 4H-imidazo-[1,2-a]-pyridine (**9a**) to 1-azaindolizine (**10a**)

Derivative **9a** (168 mg, 0.5 mmol) was dissolved in 15 ml of acetone or THF. While stirring the red-violet solution, 1 equiv of a 0.06 M aqueous solution of sodium dithionite was added. The colour of the reaction mixture changes to yellow brown, which indicates the formation of the 1-azaindolizine **10a**. The reduction product was isolated by removing the organic solvents under reduced pressure, extracting the indolizine from the aqueous layer with methylene chloride, drying the organic layer with anhydrous sodium sulfate and evaporating to dryness.

4.3.1. N^2,N^3 -Di-*p*-tolyl-imidazo-[1,2-a]-pyridine-2,3-diamine (**10a**)

Yield: 100%, yellow brown powder; ^1H NMR (250 MHz, acetone- d_6): δ 2.21 (s, 6H), 6.81 (d, $^3J=8.5$ Hz, 4H), 6.9–7.2 (m, 7H), 7.57 (t, 1H); MS (DEI): m/z (%): 328 (M^+) (85), 268 (67), 237 (51), 220 (95), 205 (100), 133 (51), 118 (42), 107 (81), 91 (76), 71 (64), 42 (78); UV–vis (THF) λ_{max} (log ϵ): 375 (3.9) nm; Fluorescence (THF, 382 nm) $\lambda_{\text{max,em}}$: 470 nm. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_4$: C, 76.80; H, 6.14; N, 17.06. Found: C, 76.78; H, 6.23; N, 16.99.

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References and notes

- Burgess, K.; Gibbs, R. U.S. Patent 6,340,750, 2002; Tsien, R. Y.; Gonzales, J. E. U.S. Patent 7,087,416, 2006.
- Langhals, H. U.S. Patent 5,693,808, 1997; U.S. Patent 5,508,137, 1996.
- Auberson, Y. Patent No. WO 2003/074519, 2003.
- Phillips, E. D. Patent No. WO 1999/048961, 1999; U.S. Patent 6,734,235, 2004.
- Atzrodt, J.; Brandenburg, J.; K  pplinger, C.; Beckert, R.; G  rls, H.; Fabian, J. *J. Prakt. Chem.* **1997**, 339, 729.
- Matschke, M.; Beckert, R. *Molecules* **2007**, 12, 723.
- Matschke, M.; K  pplinger, C.; Beckert, R. *Tetrahedron* **2006**, 60, 8586.
- Blumhoff, J.; Beckert, R.; Walther, D.; Rau, S.; Rudolph, M.; G  rls, H.; Plass, W. *Eur. J. Inorg. Chem.* **2007**, 3, 481.
- Matschke, M.; Knop, K.; Beckert, R. *Struct. Chem.*, 2008. doi:10.1007/s 11224-008-9294-y
- Beckert, R.; Hippus, C.; Gebauer, T.; St  ckner, F.; L  digk, C.; Wei  , D.; Raabe, D.; G  nther, W.; G  rls, H. *Z. Naturforsch.* **2006**, 61b, 437.
- M  ller, D.; Beckert, R.; Weston, J.; G  nther, W.; G  rls, H.; Friedrich, M. *Eur. J. Org. Chem.* **2001**, 4551.
- Bauer, K. *Chem. Ber.* **1950**, 83, 10.
- Adler, A. D.; Longo, F.; Shergalis, W. *J. Am. Chem. Soc.* **1964**, 86, 3145.
- Adler, A. D.; Longo, F.; Finarelli, J.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, 32, 476.
- Sen, R.; Sinha, N. *J. Am. Chem. Soc.* **1923**, 45, 2984.
- Jiao, G.; Thoresen, L.; Burgess, K. *J. Am. Chem. Soc.* **2003**, 125, 14668.
- Staab, H.; Sauer, M. *Liebigs Ann. Chem.* **1984**, 4, 742.
- Murdock, K. C.; Child, R. G.; Fabio, P. F.; Angier, R. B.; Wallace, R. E.; Durr, F. E.; Citarella, R. V. *J. Med. Chem.* **1979**, 22, 1024.
- Sasaki, H.; Ueno, A.; Osa, T. *Bull. Chem. Soc. Jpn.* **1988**, 61, 2321.
- Witkop, B.; Fiedler, H. *Liebigs Ann. Chem.* **1947**, 558, 91.
- Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Pechy, P.; Takata, M.; Miura, H.; Uchida, S.; Gr  tzel, M. *Adv. Mater.* **2006**, 9, 1202.
- Gebauer, T.; Beckert, R.; Wei  , D.; Knop, K.; K  pplinger, C.; G  rls, H. *Chem. Commun.* **2004**, 1860.
- Atzrodt, J.; Beckert, R.; G  nther, W.; G  rls, H. *Eur. J. Org. Chem.* **2000**, 8, 1661.
- Langer, P.; Wuckelt, J.; D  ring, M.; G  rls, H. *Eur. J. Org. Chem.* **2001**, 1503.
- Ollis, W. D.; Ramsden, C. A.; Sanforth, S. P. *Tetrahedron* **1985**, 41, 2239.
- Katritzky, A. R.; Burton, R. D.; Shipkova, P. A.; Qi, M.; Watson, C. H.; Eyler, J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 835.
- Brandenburg, J.; K  pplinger, C.; Beckert, R. *Synthesis* **1996**, 1302.
- Malhotra, S. S.; Whiting, M. C. *J. Chem. Soc.* **1960**, 3812.
- M  ller, D.; Beckert, R.; G  rls, H. *Synthesis* **2001**, 4, 601.