



# Bis-4*H*-imidazoles–tetraazafulvalenes–2,2′-biimidazoles: three variations of one redox system

M. Matschke, C. K apflinger and R. Beckert\*

*Institute of Organic and Makromolekular Chemistry, Friedrich-Schiller University, Humboldt Street 10, D-07743 Jena, Germany*

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**Abstract**—The reversibility of the two-electron reduction of tetraazafulvalenes **1** could be confirmed by employing cyclovoltammetric measurements. However, attempts to oxidize these systems electrochemically, as well as by oxidizing agents, failed. In contrast, the bis-vinylogous derivatives **2** proved to be multi-step redox systems showing two-reversible reduction as well as oxidation waves. The chemically initiated oxidation of **2** yielded the bis-4*H*-imidazoles **6**. In the presence of an excess of the oxidizing agent they dimerized and formed the deep blue colored derivative **7a**. Treatment of the phenylogous systems **8** with sodium dithionite provided a new entry to quinomethides of type **9**, which can be stabilized towards oxygen by cyclization reaction to give the pigment-like bis-urea **11**. Derivative **9** represents the SEM form of this four-step redox system and thus can finally be reduced to yield the tetraaminosubstituted biimidazoles **12**. Based on these findings, the close correlation among bis-4*H*-imidazoles (OX), tetraazafulvalenes (SEM), and tetraaminosubstituted biimidazoles (RED) could be demonstrated. Due to the fact that tetraazafulvalenes constitute stable closed-shell SEM systems, their intense UV–vis absorptions can now be explained and related to their redox behavior.

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## 1. Introduction

Electrochromic behavior is mainly based on two-step redox systems for which H unig and others have developed a new principle.<sup>1,2</sup> In the field of advanced materials, the so-called violenes,<sup>3</sup> which are the radical ions SEM<sup>+/-</sup>, always represent the species with the longest wavelength absorptions and highest extinction coefficients within the redox system. Their color intensity is closely related to the thermodynamic stability for which the semiquinone formation constant ( $K_{SEM}$ ) is the most commonly applied value. Recently, the synthesis and electrochemical characterization of boratetraazapentalenes derived from 4*H*-imidazoles **1** was reported.<sup>4</sup> The radical anions of this new class of electrophores show unusual high values of  $K_{SEM}$  (up to  $10^{15}$ ). Since radical reactions often have low activation barriers, these open-shell species tend to decompose more rapidly than closed-shell systems. We therefore focused our work on the development of redox systems in which the radical SEM state is replaced by closed-shell moieties.

Tetraazafulvalenes **2** and their bis-vinylogous derivative **3** represent a novel class of cross-conjugated heterocyclic compounds for which different syntheses have been developed in our laboratories. Due to the secondary arylamino

groups, further derivatization can be realized by a large variety of alkylation/acylation, cyclization, and cross-coupling procedures.<sup>5–8</sup> Their long wavelength absorptions in the UV–vis spectra together with high extinction coefficients ( $\log \epsilon > 4$ ) make them promising candidates for the construction of functional dyes.<sup>9</sup>

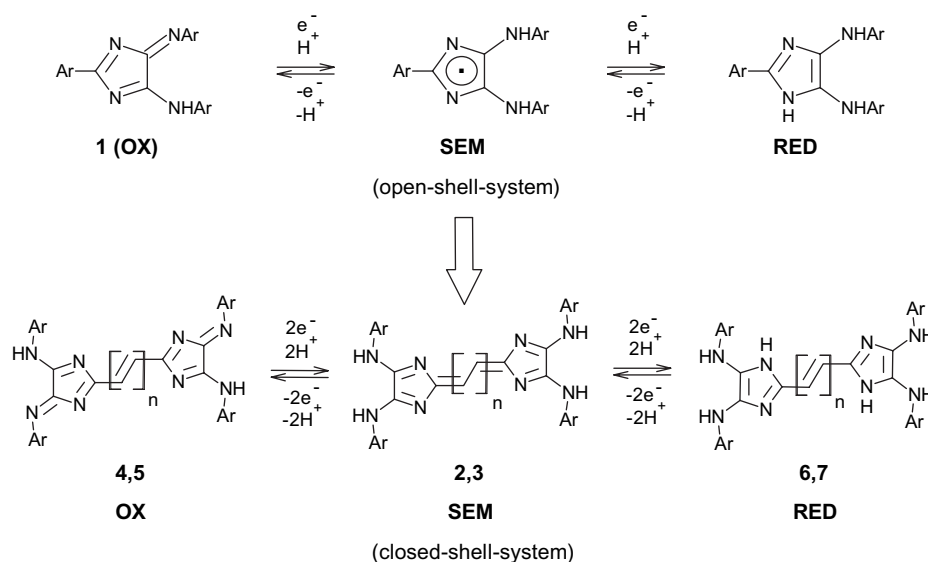
In principle, the electron-poor heterocyclic part of **2** enables them to be the electronic counterpart of tetrathiafulvalenes and in addition, offers the ability for the synthesis of charge-transfer complexes with such donor molecules.<sup>10</sup> On the other hand, tetraazafulvalenes can easily be reduced to yield 4,4′,5,5′-tetraaminosubstituted 2,2′-biimidazoles **6**. These electron-rich heterocycles can also be regarded as leuco-forms of **2** and immediately reoxidize in the presence of air oxygen to its starting material (Scheme 1). The greenish fluorescent derivatives **6** can be stabilized under strictly anaerobic conditions by acylation reactions with  $Boc_2O$  or  $CF_3CH_2SO_2Cl$ .<sup>11</sup>

## 2. Results and discussion

Due to its inherent merocyanine type system, **3** is supposed to behave as a multi-step redox system according to Scheme 1. We could recently<sup>11</sup> demonstrate that tetraazafulvalenes **3** behave as electrophores, which can easily be switched between oxidized and reduced form. In the first step, most probably the radical anion would be generated. The second

**Keywords:** bis-4*H*-Imidazoles; Tetraazafulvalenes; Biimidazoles; Four-electron redox system; Quinomethides.

\* Corresponding author. Tel.: +49 3641 948230; fax: +49 3641 948212; e-mail: [c6bera@uni-jena.de](mailto:c6bera@uni-jena.de)



**Scheme 1.** Compounds **2**, **4**, and **6**:  $n=0$ ; **3**, **5**, and **7**:  $n=1$ .

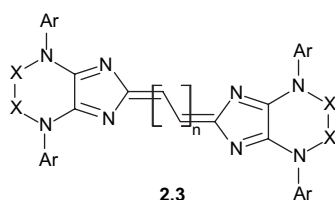
electron transfer step leads to the formation of the dianion, which is immediately protonated by water to yield the 2,2'-biimidazoles of type **7**. Now, both consecutive single-electron transfer processes could be recorded by electrochemical measurements. Employing difference pulse polarographic measurements, two peaks can be clearly ascribed to two different single-electron transfer steps. The quasi-reversibility of the reduction was confirmed by cyclic voltammetric measurements ( $\Delta E_{\text{RED,OX}}^{1,2} > 0.059$  V). The redox potentials and semiquinone formation constants  $K_{\text{SEM}}$  of selected tetraazafulvalenes are listed in Table 1. Compared to other acceptor molecules such as tetracyanoquinodimethane (TCNQ) or  $N,N'$ -dicyanoquinodimines (DCNQI)<sup>12</sup> with  $K_{\text{SEM}}$  values in the range of  $10^7$ – $10^{11}$ , the tetraazafulvalenes show rather small parameters ( $10^2$ – $10^{11}$ ).

The data also demonstrates the small influence of the substituted aryl groups, the bonding mode of the two imidazoles ( $n=0,1$ ), as well as the nature of an additional ring fusion on the reduction potential.

The oxidation reaction of **2** provides the possibility of obtaining derivatives of type **4**, in which two 4*H*-imidazoles are directly connected via a single bond. The cyclic voltammogram of **2b** (Ar=4-Tol) showed two irreversible oxidation waves at positive potentials. These findings were in agreement with the results obtained by using a series of oxidation reagents. All attempts to chemically oxidize **2** yielded polymeric material and only small amounts of isocyanides and derivatives of parabanic acid. The latter resulted from a direct oxidative cleavage of the central double bond of **2**. The independent synthesis of **4** starting from oxalyl chloride and oxalic amidines<sup>13</sup> was unsuccessful and proved to be an additional evidence for the instability of the bis-4*H*-imidazoles **4**.

In further experiments we therefore studied the redox behavior of the easily accessible tetraazafulvalenes **3**. Such vinyllogous derivatives should show a similar redox chemistry as their parent compound **2**. The cyclic voltammograms, as well as the difference pulse polarographic measurements

**Table 1.** Reduction potentials  $E_{\text{RED}}^1$ ,  $E_{\text{RED}}^2$ , and  $K_{\text{SEM}}$  of **2** and **3**



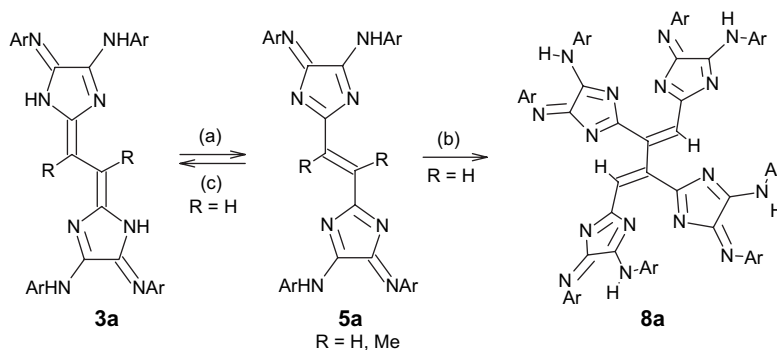
Compound	$n$	Ar	X–X	$E_{\text{RED}}^1$ (V)	$E_{\text{RED}}^2$ (V)	$K_{\text{SEM}}$
<b>2a</b>	0	4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub>	H, H	–0.669	–0.786	9.6E+001
<b>2b</b>	0	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H, H	–0.775	–1.050	1.5E+005
<b>2c</b>	0	4-I-C <sub>6</sub> H <sub>4</sub>	H, H	–0.648	–0.781	1.8E+002
<b>2d</b>	0	4-Br-C <sub>6</sub> H <sub>4</sub>	H, H	–0.762	–0.961	2.4E+003
<b>2e</b>	0	4-Cl-C <sub>6</sub> H <sub>4</sub>	H, H	–0.861	–1.133	4.1E+004
<b>2f</b>	0	4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub>	–CH=CH–	–0.570	–1.251	3.5E+011
<b>2g</b>	0	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	–C=C–     CN CN	–1.375	–1.625	1.7E+004
<b>2h</b>	0	4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub>	>CH(OEt)	–0.762	–1.050	7.6E+004
<b>3a</b>	1	4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub>	H, H	–0.654	–1.043	3.9E+006
<b>3b</b>	1	4-Br-C <sub>6</sub> H <sub>4</sub>	H, H	–0.693	–0.825	1.7E+002

of **3a** and **3b**, reveal two completely reversible reduction waves, which correspond to two single-electron transfer steps. This reduction of **3** yielded their leuco-forms **7**, which could also be obtained by ultrasound irradiation of **3** in THF in the presence of small amounts of aqueous sodium dithionite. Employing metallic lithium, this chemically induced reduction of derivatives **3** was already used for the preparation of stilbenoid biimidazoles.<sup>5</sup> However, in derivatives **3**, two-reversible oxidation waves (**3a**:  $E_{\text{OX}}^1=0.566$  V,  $E_{\text{OX}}^2=0.879$  V; **3b**:  $E_{\text{OX}}^1=0.664$  V,  $E_{\text{OX}}^2=0.908$  V) promise an entry to stable oxidation products of type **5** (Scheme 1), which are not accessible via tetraazafulvalenes **2**.

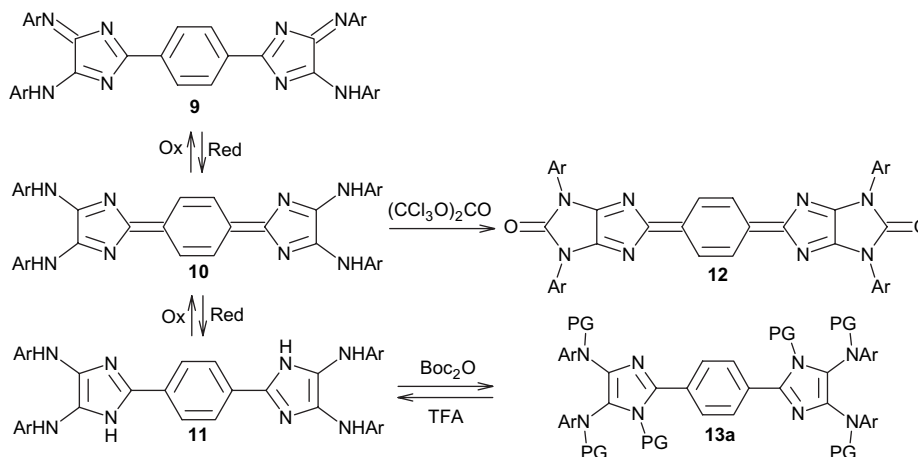
The chemical initiated oxidation of **3** has also been succeeded by using several oxidizing agents (DDQ,  $\text{Cu}^{2+}$ /pyridine, iodosobenzene bis-trifluoroacetate, 1,4-benzoquinone, cerium(IV) ammonium nitrate). In all cases studied the oxidation products were purified by column chromatography and identified as bis-4*H*-imidazoles **5**. These deep red compounds are stable up to 50 °C; at higher temperatures and in the presence of an excess of oxidizing agent they were transformed into deep blue compounds. By means of MS and NMR spectroscopy, derivative **8a** (Ar=4-*t*-BuPh) was characterized as a dimerization product derived from the corresponding bis-4*H*-imidazole **5a**. This somewhat surprising dimerization probably took place via cationic radical intermediates<sup>14</sup> formed by oxidation of the exocyclic methine groups of **5** (R=H). Derivatives in which the methine hydrogens are replaced by methyl groups (R=CH<sub>3</sub>)<sup>14</sup>

did not show such oxidative dimerization reactions (Scheme 2).

We have now expanded our research to consider the redox chemistry of bifunctional, ‘phenylogous’ 4*H*-imidazoles<sup>4</sup> with those of tetraazafulvalenes. These molecules can easily be obtained via two different pathways<sup>13,15</sup> and are stable crystalline compounds. Due to their low solubilities in solvents used for CV measurements, only chemically induced redox reactions were studied. Thus, upon treatment of bis-4*H*-imidazoles **9** with sodium dithionite, the color of the solution turned from red to blue. Purification of the reaction mixture by flash chromatography under argon yielded deep blue stable substances, but upon exposure to air a fast reoxidation to the starting material was observed. The spectral data (NMR and MS) of **10** was in agreement with the structural assignment presented in Scheme 3. The UV–vis spectrum of **10** exhibited a strong absorption at long wavelengths ( $\lambda_{\text{max}}$  (log  $\epsilon$ ): **10a**: 634 (4.4); **10b**: 633 (4.2)), which is characteristic for such quinoid compounds.<sup>16–19</sup> Since no radical species could be detected by ESR, the quinoid structure of **10** could be achieved by electron coupling of both parts of the peripheric reduced heterocycles. Derivative **10** constitutes the first tetraaminosubstituted quinomethide and can be regarded as a hybrid between tetraazafulvalenes and quinodimethides. The cyclization of **10** with triphosgene formed the deep purple bis-urea **12**, which showed pigment-like properties and was stable towards oxygen. The reduction



**Scheme 2.** Compounds **3a**, **5a**, and **8a**: Ar=4-*t*-C<sub>4</sub>H<sub>9</sub>-Ph; Reaction conditions: (a) 1 equiv DDQ, 5 min, rt, yield 45%; (b) 1 equiv DDQ, 18 h, rt, yield 50% and (c) 0.06 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, ultrasound irradiation, 15 min, rt, yield 92%.



**Scheme 3.** Compounds **9–12a**: Ar=4-*t*-C<sub>4</sub>H<sub>9</sub>-Ph; **b**: Ar=4-*n*-C<sub>6</sub>H<sub>13</sub>-Ph; **13a**: Ar=4-*t*-C<sub>4</sub>H<sub>9</sub>-Ph, PG=Boc.

of **10** with an excess of sodium dithionite finally lead to phenylogous 2,2'-biimidazoles of type **11** (Scheme 3).

These derivatives possess two-electron-rich 4,5-diaminoimidazoles and are therefore only stable if air is strictly excluded. The stabilization of **11a** can be realized via acylation reaction with Boc<sub>2</sub>O to yield the greenish fluorescent derivative **13a**. The deprotection of this conserved leuco-form with trifluoroacetic acid reproduced the bis-imidazole **11a**, which reoxidized immediately in the presence of air to revert back to **9a**. No formation of stable charge-transfer complexes was observed with para benzoquinone. In a smooth reaction, only oxidation took place and yielded the starting material **9**.

### 3. Experimental

#### 3.1. General

All reactions were monitored by TLC, carried out on 0.25 mm Merck silica gel plates (60F<sub>254</sub>) using UV light. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DRX 400 or Bruker AC 250 spectrometer. Melting points are measured with a Galen TM3 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. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932. The tetraazafulvalenes **2**,<sup>6,8</sup> and **3**<sup>14,20,21</sup> were prepared according to literature procedures. Electrochemical measurements were carried out with a Metrohm 663VA Stand using mercury or platinum electrodes and tetrabutylammoniumhexafluorophosphate as conductive salt.

**3.1.1. (syn, anti)-5,5'-Diethoxy-4,6,4',6'-tetrakis(4-tert-butylphenyl)-5,6,5',6'-tetrahydro-4H,4'H-[2,2']bis(imidazo[4,5]imidazolyliidene) (2h).** Yield: 52%, metallic green crystals, mp > 300 °C; <sup>1</sup>H NMR (250 MHz, THF): δ 1.01 (t, J=6.9 Hz, 6H), 1.36 (s, 36H), 3.35 (d, J=7.8 Hz, 4H), 7.48 (d, J=8.7 Hz, 8H), 8.04 (d, J=8.7 Hz, 8H); <sup>13</sup>C NMR (250 MHz, THF): δ 11.5, 28.5, 31.8, 53.2, 100.5, 114.6, 123.5, 132.5, 143.9, 155.0, 157.8; MS (DCI with H<sub>2</sub>O): *m/e* (%): 833 (M+1)<sup>+</sup> (100), 786 (21), 775 (11), 728 (31), 671 (10), 480 (98), 428 (25), 333 (48), 186 (13), 147 (61), 133 (42), 57 (28); UV–vis (THF) λ<sub>max</sub> (log ε): 431 (4.4), 458 (4.7), 490 (4.8) nm; Fluorescence (THF, 340 nm): λ<sub>max,em</sub>: 509, 562 nm; Anal. calcd for C<sub>52</sub>H<sub>64</sub>N<sub>8</sub>O<sub>2</sub>: C, 74.97; H, 7.74; N, 13.45. Found: C, 74.90; H, 7.79; N, 13.49.

#### 3.2. Reduction of the tetraazafulvalenes of type (3)<sup>11</sup>

**3.2.1. 2-[2-[4,5-Bis-(4-tert-butylphenylamino)-1H-imidazol-2-yl]-vinyl]-N<sup>4</sup>,N<sup>5</sup>-bis-(4-tert-butylphenyl)-1H-imidazol-4,5-diamine (7a).** Yield: 94%, brownish solid; <sup>1</sup>H NMR (250 MHz, THF): δ 1.19 (s, 36H), 6.55 (d, J=8.7 Hz, 8H), 7.01 (d, J=8.7 Hz, 8H); UV–vis (THF) λ<sub>max</sub>: 387 nm; Fluorescence (THF, 340 nm) λ<sub>max,em</sub>: 515 nm; C<sub>48</sub>H<sub>60</sub>N<sub>8</sub> (748.5).

**3.2.2. 2-[2-[4,5-Bis-(4-bromophenylamino)-1H-imidazol-2-yl]-vinyl]-N<sup>4</sup>,N<sup>5</sup>-bis-(4-bromophenyl)-1H-imidazol-4,5-diamine (7b).** Yield: 92%, brownish solid; <sup>1</sup>H NMR

(250 MHz, THF): δ 7.06 (d, J=8.8 Hz, 8H), 6.53 (d, J=8.8 Hz, 8H); UV–vis (THF) λ<sub>max</sub>: 405 nm; Fluorescence (THF, 340 nm) λ<sub>max,em</sub>: 534 nm; C<sub>32</sub>H<sub>24</sub>Br<sub>4</sub>N<sub>8</sub> (840.2).

#### 3.3. General procedure for the oxidation of tetraazafulvalenes of type (3)

A mixture of **3** (0.1 mmol), 30 ml of THF, and 0.1 mmol DDQ was stirred at rt for about 10 min. The solvent was removed in vacuo and the crude product **5** was purified by column chromatography (SiO<sub>2</sub>, toluene/acetone 9:1).

**5a:** Yield: 45%, red solid, mp 260 °C (decomp.); <sup>1</sup>H NMR (250 MHz, THF): δ 1.37 (s, 36H), 7.49 (m, 16H), 8.06 (s, 2H); <sup>13</sup>C NMR (250 MHz, THF): δ 28.8, 32.4, 117.6, 123.2, 123.4, 123.6, 126.0, 126.8, 134.6, 135.6, 141.3, 147.8; MS (DCI with H<sub>2</sub>O): *m/e* (%): 745 (M)<sup>+</sup> (1), 613 (4), 508 (50), 466 (46), 389 (10), 353 (12), 307 (30), 251 (6), 176 (14), 160 (66), 150 (100), 134 (44), 94 (30); UV–vis (THF) λ<sub>max</sub> (log ε): 451 (4.2), 479 (4.2), 533 (4.2) nm; CV: E<sub>OX</sub><sup>1</sup>=0.566 V, E<sub>OX</sub><sup>2</sup>=0.879 V; C<sub>48</sub>H<sub>56</sub>N<sub>8</sub> (745.04).

**5b:** Yield: 42%, red solid, mp 258 °C; <sup>1</sup>H NMR (250 MHz, THF): δ 6.91 (s, 2H), 7.08–7.20 (m, 16H); <sup>13</sup>C NMR (250 MHz, THF): δ 117.5, 122.3, 123.1, 124.9, 125.0, 127.9, 128.7, 131.4, 137.2, 137.4, 147.0, 147.7, 151.7; MS (CI): *m/e* (%): 837 (M+1)<sup>+</sup> (4), 803 (35), 558 (50), 471 (60), 429 (66), 413 (100), 349 (38), 309 (40), 291 (61), 223 (18), 81 (24); UV–vis (THF) λ<sub>max</sub> (log ε): 231 (4.1), 288 (4.2), 526 (4.3) nm; CV: E<sub>OX</sub><sup>1</sup>=0.664 V, E<sub>OX</sub><sup>2</sup>=0.908 V; C<sub>32</sub>H<sub>20</sub>N<sub>8</sub>Br<sub>4</sub> (836.34).

#### 3.4. Procedure for the preparation of the dimer (8a)

Compound **5a** (0.05 mmol) was dissolved in 20 ml of THF. After addition of 0.05 mmol DDQ, the reaction mixture was stirred at rt for 18 h. After removing the solvent in vacuo, the dimer **8a** was purified by column chromatography (SiO<sub>2</sub>, toluene/acetone 9:1).

**8a:** Yield: 50%, dark blue solid, mp 254 °C; <sup>1</sup>H NMR (250 MHz, THF): δ 1.21 (s, 18H), 1.29 (s, 18H), 1.32 (s, 18H), 1.36 (s, 18H), 6.83 (d, J=8.5 Hz, 4H), 7.06 (d, J=8.5 Hz, 4H), 7.12 (d, J=8.5 Hz, 4H), 7.17 (d, J=8.5 Hz, 4H), 7.28 (d, J=8.5 Hz, 4H), 7.36 (d, J=8.5 Hz, 4H), 7.40 (d, J=8.5 Hz, 4H), 7.85 (d, J=8.5 Hz, 4H), 8.44 (s, 2H), 8.64 (s, 2H); <sup>13</sup>C NMR (250 MHz, THF): δ 30.5, 33.5, 117.7, 118.2, 119.3, 125.2, 135.4, 137.1, 145.3, 148.4, 150.4, 157.2; MS (DCI with H<sub>2</sub>O): *m/e* (%): 1490 (M)<sup>+</sup> (80), 1342 (100), 1130 (10), 985 (4), 894 (12), 833 (30), 721 (8), 508 (14), 231 (8), 217 (8), 131 (8); UV–vis (THF) λ<sub>max</sub> (log ε): 228 (4.9), 286 (4.7), 529 (4.5), 571 (4.7), 623 (4.6) nm; C<sub>96</sub>H<sub>114</sub>N<sub>16</sub> (1490.08).

#### 3.5. Reduction of bis-4H-imidazoles (9) to quinomethides (10)

Derivative **9** (0.1 mmol) dissolved in THF was reduced with a 0.06 M sodium dithionite solution (1 equiv). The deep blue colored quinomethides **10** were obtained after removing the solvent in vacuo.

**10a:** Yield: 94%, dark blue solid;  $^1\text{H NMR}$  (400 MHz, THF):  $\delta$  1.27 (s, 36H), 6.84 (d,  $J=8.8$  Hz, 8H), 7.31 (d,  $J=8.8$  Hz, 8H), 8.06 (s, 4H); HRMS (DEI):  $m/z$  calcd for  $\text{C}_{52}\text{H}_{60}\text{N}_8$  ( $\text{M}$ ) $^+$ : 796.4941, found: 796.5030; UV–vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 634 (4.4) nm.

**10b:** Yield: 95%, dark blue solid;  $^1\text{H NMR}$  (250 MHz, THF):  $\delta$  0.78 (t,  $J=8.0$  Hz, 12H), 1.20 (m, 24H), 1.45 (m, 16H), 6.55 (d,  $J=8.5$  Hz, 8H), 6.77 (d,  $J=8.5$  Hz, 8H), 7.97 (s, 4H); HRMS (DEI):  $m/z$  calcd for  $\text{C}_{60}\text{H}_{76}\text{N}_8$  ( $\text{M}$ ) $^+$ : 908.6035, found: 908.6040; UV–vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 633 (4.0) nm.

### 3.6. Cyclization of the quinomethides (10) with triphosgene to bis-urea derivatives (12)

Compound **10** (0.1 mmol) and 0.25 mmol of triphosgene were dissolved under argon in 20 ml of dry toluene. The reaction mixture was then heated under reflux for 5 h. After completion of the reaction the cyclic bis-urea derivatives were separated by addition of a mixture of water/acetone (1:1) as deep purple pigment-like solids, which were filtered off and dried in vacuo.

**12a:** Yield: 30%, purple, metallic-shining microcrystals, mp 280 °C (decomp.);  $^1\text{H NMR}$  (250 MHz, THF):  $\delta$  1.29 (s, 36H), 7.05 (s, 4H), 7.42 (d,  $J=8.5$  Hz, 8H), 7.54 (d,  $J=8.5$  Hz, 8H); MS (DCI with  $\text{H}_2\text{O}$ ):  $m/e$  (%): 849 ( $\text{M}$ ) $^+$  (22), 793 (2), 424 (6), 379 (10), 323 (2), 176 (100), 159 (26), 123 (28), 109 (22), 93 (15); IR (KBr): 2963, 2906, 2868, 1754, 1624, 1517, 1437, 1406, 1266, 1107, 1088, 1034, 978, 877, 831, 802, 693, 667  $\text{cm}^{-1}$ ; UV–vis (THF)  $\lambda_{\text{max}}$ : 475, 556 nm;  $\text{C}_{54}\text{H}_{56}\text{N}_8\text{O}_2$  (848.45).

**12b:** Yield: 34%, purple, metallic-shining microcrystals, mp 300 °C (decomp.);  $^1\text{H NMR}$  (400 MHz, THF):  $\delta$  0.92 (t,  $J=8.0$  Hz, 12H), 1.36 (m, 32H), 2.70 (t,  $J=8.0$  Hz, 8H), 7.38 (d,  $J=8.5$  Hz, 8H), 8.05 (d,  $J=8.5$  Hz, 8H), 8.15 (s, 4H); MS (DCI with  $\text{H}_2\text{O}$ ):  $m/e$  (%): 961 ( $\text{M}+1$ ) $^+$  (4), 745 (12), 584 (16), 407 (12), 309 (8), 204 (100), 178 (59), 132 (27), 106 (13); IR (KBr): 2922, 2854, 1751, 1621, 1512, 1484, 1403, 975  $\text{cm}^{-1}$ ; UV–vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 246 (4.4), 560 (4.8) nm;  $\text{C}_{62}\text{H}_{72}\text{N}_8\text{O}_2$  (960.58).

### 3.7. Reduction of the quinomethides (10) to biimidazoles (11)

Derivative **10** (0.1 mmol), dissolved in 20 ml of THF was reduced with 5 ml of 0.06 M solution of sodium dithionite. The reaction mixture was irradiated with ultrasound for 10 min at rt. The biimidazoles **11** were obtained as yellow solids by removing the solvent in vacuo.

**11a:** Yield: 96%, yellow solid;  $^1\text{H NMR}$  (250 MHz, THF):  $\delta$  1.24 (s, 36H), 6.82 (d,  $J=8.3$  Hz, 8H), 7.29 (d,  $J=8.3$  Hz, 8H), 8.04 (s, 4H); UV–vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 317 (4.4), 370 (4.5) nm;  $\text{C}_{52}\text{H}_{62}\text{N}_8$  (798.48).

**11b:** Yield: 97%, yellow solid;  $^1\text{H NMR}$  (250 MHz, THF):  $\delta$  0.79 (t,  $J=8.0$  Hz, 12H), 1.20 (m, 24H), 1.45 (m, 16H), 6.51 (d,  $J=8.5$  Hz, 8H), 7.09 (d,  $J=8.5$  Hz, 8H), 7.863 (s,

4H); UV–vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 317 (4.3), 375 (4.4) nm;  $\text{C}_{60}\text{H}_{78}\text{N}_8$  (910.60).

### 3.8. Derivative (13a) was prepared according to the literature procedure<sup>11</sup>

**13a:** Yield: 15%, brownish solid;  $^1\text{H NMR}$  (250 MHz, THF):  $\delta$  1.17 (s, 18H), 1.22 (s, 36H), 1.29 (s, 36H), 7.24 (d,  $J=8.8$  Hz, 8H), 7.70 (m, 12H); MS (micro-ESI, acetone/methanol):  $m/e$  (%): 1399 ( $\text{M}$ ) $^+$  (36), 1299 (12), 1199 (14), 1100 (8), 1001 (6), 901 (8), 800 (4), 775 (8), 623 (10), 471 (20), 413 (100), 301 (10); IR (KBr): 2966, 2871, 1758, 1717, 1611, 1515, 1477, 1392, 1367, 1325, 1302, 1145, 1107, 836  $\text{cm}^{-1}$ ; UV–vis (THF)  $\lambda_{\text{max}}$ : 271, 296, 335 nm.

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