Novel Disubstituted Phenylene-Linked Bis-imidazole Derivatives: Facile Synthesis and Optical Properties

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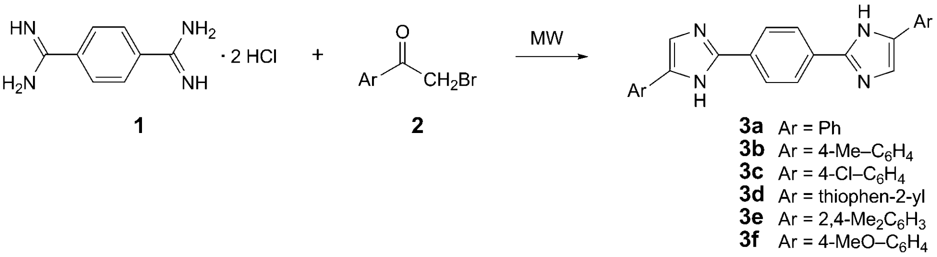
Six novel disubstituted phenylene-linked bis-imidazole derivatives, **3a**–**3f**, were prepared by a one-pot, microwave-assisted method under solvent-free conditions, in yields ranging from 61.6 to 85.6%. The new compounds were characterized by ^{1}H- and ^{13}C-NMR, UV/VIS, and fluorescence spectroscopy, and mass spectrometry, as well as by elemental analyses. The influence of substituents and solvents on the optical properties of **3a**–**3f** was investigated. It was found that there is little influence on absorption and excitation spectra in contrast to emission spectra. Compounds **3a**–**3f** exhibit strong fluorescence in solution, their fluorescence quantum yields ranging from 0.27 to 0.96.

Introduction. – New molecular fluorophores, which play an important role in fluorescence sensors [1–3], fluorescence imaging [4][5], and fluorescence switching [6–8], have recently attracted great interest in the analysis of biological systems [9–13] and optical applications [14–18]. Among these molecular fluorophores, phenylene-linked bis-imidazole derivatives have been used due to their unique optical properties [19–21]. In addition, they can be used in two-photon fluorescence and as pH probe [22][23]. To the best of our knowledge, several reports on the synthesis and on the physical properties of tetrasubstituted phenylene-linked bis-imidazole compounds have been published [24–29], and the synthesis of phenylene-linked bis-imidazole compounds was only accomplished by condensation of 1,2-dicarbonyl compounds and aldehydes with NH_3. However, to our surprise, studies on the synthesis and optical properties of disubstituted phenylene-linked bis-imidazole compounds were limited. In 1975, *Mahadik* and *Sunthankar* [30] reported the synthesis of some *N*,*N*′-disubstituted phenylene-linked bis-imidazoles with yields of 50–60%. Since then, there were no reports on these compounds, except for the one of *Jadhav* and co-workers [24] in 2008, who described the synthesis of 2,2′-(1,4-phenylene)bis[5-phenyl-1*H*-imidazole] only, without giving any optical properties. Considering the above reports, the synthesis of novel disubstituted phenylene-linked bis-imidazoles and the study of the underlying structure–property relationships was a challenge.

In this article, a microwave-assisted and solvent-free method for the synthesis of 5-aryl-substituted phenylene-linked bis-imidazoles is reported, involving condensation of benzene-1,4-dicarboximidamidium dichloride with 1-aryl-2-bromoethanones in the presence of using $KHCO_3$ as acid-binding agent. The six novel disubstituted phenylene-linked bis-imidazole derivatives **3a**–**3f** were synthesized, characterized, and their optical properties investigated.

Results and Discussion. – *Synthesis and Characterization.* Monoimidazoles have already been prepared with an efficient procedure by using benzamidine hydrochloride monohydrate and 1-aryl-2-bromoalkan-1-ones as substrates [31–36]. According to these method, disubstituted phenylene-linked bis-imidazole derivatives were obtained with quite low yields after refluxing for 72 h and purification by silica-gel column chromatography (*e.g.*, for compound **3a** only 30% yield). Considering that the microwave-assisted synthesis method has been efficient in some condensation reactions [37–39], an improved method for synthesis of **3a**–**3f** was elaborated successfully under solvent-free conditions by microwave irradiation. Under the microwave-assisted conditions, the reaction time to yield, *e.g.*, **3a** was dramatically reduced from the 72 h in the conventional heating to just a few minutes. More important, the starting materials and by-products in the crude products were easily removed by washing with hot brine followed by recrystallization from MeOH/THF 1:1. The desired products **3a**–**3f** were thus obtained in 61.6–85.6% yields (*Scheme*). The improved method is an environmentally friendly and effective procedure for the synthesis of disubstituted phenylene-linked bis-imidazoles **3**, starting from benzene-1,4-dicarboximidamidium dichloride (**1**) and 1-aryl-2-bromoethanones **2**. All the compounds were obtained as white solids, and their structure was confirmed by ^{1}H- and ^{13}C-NMR spectra, EI-MS, and elemental analyses. Compounds **3a**–**3f** were soluble in $CHCl_3$, toluene, THF, MeOH, and HCO_2H in varying degrees.

Scheme. *Synthesis of Bis-imidazole Derivatives* **3**



Photophysical Properties of **3a**–**3f** *in Solution.* The absorption spectra of the bis-imidazoles **3a**–**3f** in MeCN solution (10^{-5} M) are shown in *Fig. 1*, and the absorption properties are given in *Table 1*. There are two absorption bands at *ca.* 275 and 340 nm, and they all can be assigned to the π–π^* electron transitions by virtue of their large epsilon ($\varepsilon \approx 10^4$ M^{-1} cm^{-1}). All disubstituted phenylene-linked bis-imidazoles **3a**–**3f** have an almost identical absorption maximum ($\lambda_{\max}^{\mathrm{Abs}}$), ranging from 339 to 348 nm, which suggests that the $\lambda_{\max}^{\mathrm{Abs}}$ of these compounds mainly depends on the length of the main conjugated structure with little effect of the substituents.

The dilute-solution (10^{-5} M) fluorescence spectra of **3a**–**3f** in MeCN are shown in *Fig. 2*, and the fluorescence properties and corresponding Φ_f are given in *Table 1*. All compounds **3a**–**3f** emit blue light with an emission maximum in the range of 389.5–419.5 nm. Compared to **3a**, the alkyl-substituted **3b** and **3e** and chloro-substituted **3c** show blue-shifted emission spectra, while the thiophene-substituted **3d** and the MeO-substituted **3f** show a red shift. The largest red shift (17.5 nm) of **3d** is a result of

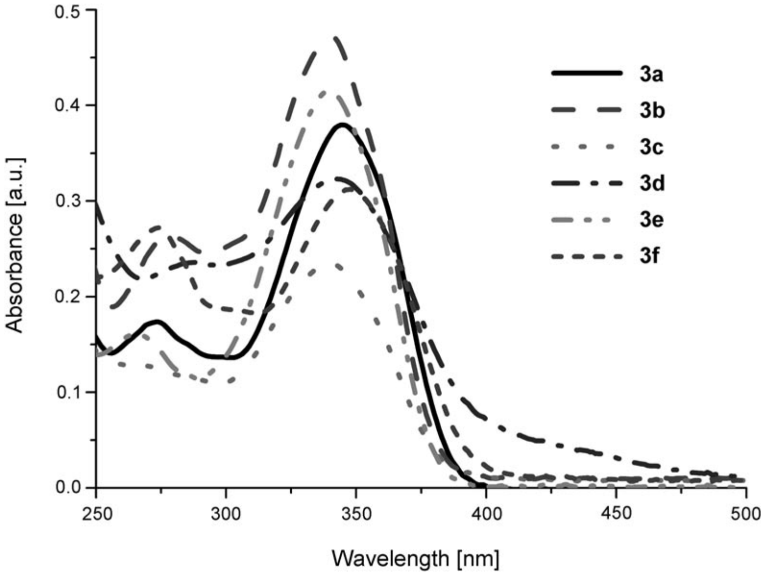


Fig. 1. *UV/VIS Absorption spectra of* **3a**–**3f** *in MeCN solution* ($c = 10^{-5}$ M)

Table 1. *UV/VIS Absorption and Fluorescence Data for* **3a**–**3f** *in MeCN* ($c = 10^{-5}$ M)

	ε [10^{-4} M^{-1} cm^{-1}]	λ_{max}^{Abs} [nm]	λ_{max}^{Ex} [nm]	λ_{max}^{Em} [nm]	*Stokes* shift [nm]	E_g^{Opt} [a]) [eV]	Φ_f [b])
3a	3.80	345	347	402.0	55.0	3.19	0.74
3b	4.73	340	338.5	392.5	54.0	3.25	0.88
3c	2.35	340	340.5	389.5	49.0	3.25	0.64
3d	3.23	348	349	419.5	70.5	3.06	0.27
3e	4.15	339	332	396.5	64.5	3.28	0.96
3f	3.12	348	348.5	414.0	65.5	3.16	0.77

[a]) Estimated from the onset of the absorption spectra ($E_g^{Opt} = 1240/\lambda_{onset}$). [b]) Determined in MeCN solution (*Abs* < 0.1) at room temperature, with 9,10-diphenylanthracene ($\Phi_f = 0.90$ in hexane) as standard.

increased electron density associated with the thiophene group and the weak intramolecular donor–acceptor interaction inducing a polarization in the electronically excited state [40]. The fluorescence quantum yield (Φ_f) of compounds **3a**–**3f** in MeCN solution is relatively high, ranging from 0.27 for **3d** to 0.96 for **3e** by using 9,10-diphenylanthracene ($\Phi_f = 0.90$ in hexane) [41] as a reference. Comparison of compound **3a** with **3b** and **3e** shows that replacing the H-atoms in *para*- or *ortho*-position by Me groups leads to an increase of Φ_f by more than 15%. Compared to **3a**, the Φ_f of **3d** is significantly lower. The low emission quantum yield of **3d** is largely due to the donor–acceptor–donor nature of this bis-imidazole, and consequently to intramolecular charge transfer, which is known as an important luminescence-quenching mechanism in such donor–acceptor systems [42]. Comparison of compound

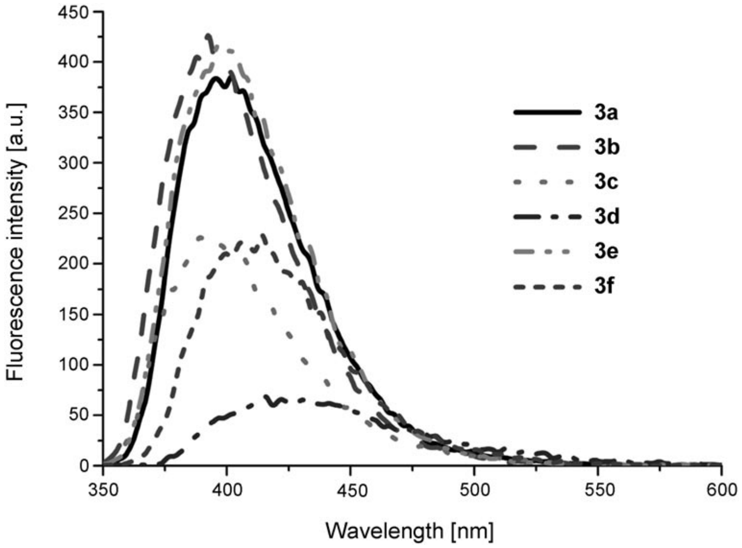


Fig. 2. *Fluorescence spectra of* **3a**–**3f** *in MeCN solution* ($c = 10^{-5}$ M)

3a with **3f** indicates that the substitution of the *para* H-atoms of the phenyl substituents by MeO groups hardly changes the fluorescence quantum yield. Comparison of compound **3a** with **3c** indicates that the substitution of the *para* H-atoms by Cl substituents leads to a slight decrease of the fluorescence quantum yield **3c**, the low value of Φ_f being the result of competing $S_1 \rightarrow T_1$ intersystem crossing because of the 'internal heavy-atom effect' [22]. Optical band gaps (E_g^{Opt}) determined by the absorption edge of the solution spectra are also given in *Table 1*, which vary from 3.06 eV in **3d** to 3.28 eV in **3e**.

Solvent Effects on the Absorption and Fluorescence Properties. The absorption and emission spectra of **3d** in various solvents, *i.e.*, in several protic (MeOH and HCO_2H) and aprotic (MeCN, acetone, $CDCl_3$, AcOEt, Et_2O, toluene, and THF) solvents, are shown in *Figs. 3* and *4*. Compound **3d** shows a pronounced change in position and intensity of the absorption or emission band accompanying a change in the polarity of the solvent. This phenomenon can also be explained by the effects of charge transfer which cause the change of color [25]. The UV/VIS absorption and fluorescence properties of **3d** in various solvents are given in *Table 2*, **3d** has a nearly identical absorption maximum ($\lambda_{\mathrm{max}}^{\mathrm{Abs}}$) (from 348 to 351 nm) and excitation maximum ($\lambda_{\mathrm{max}}^{\mathrm{Ex}}$) (from 348.5 to 354 nm) in the above nine solvents. A red shift of the emission maximum ($\lambda_{\mathrm{max}}^{\mathrm{Em}}$), which ranges from 397 nm in nonpolar solvents such as toluene, to 419.5 nm in medium-polar solvents such as MeCN, and then to 438 nm in strongly polar solvents such as MeOH. The common feature of these latter solvents is the presence of a lone pair of electrons which can form an H-bond with the N–H group of **3d**. In HCO_2H, the red shift of the emission may be the result of the excited-state protonation [26]. Phenomena of color change in different solvents of these disubstituted phenylene-linked bis-imidazoles such as **3d** were more obvious than those of the tetrasubstituted

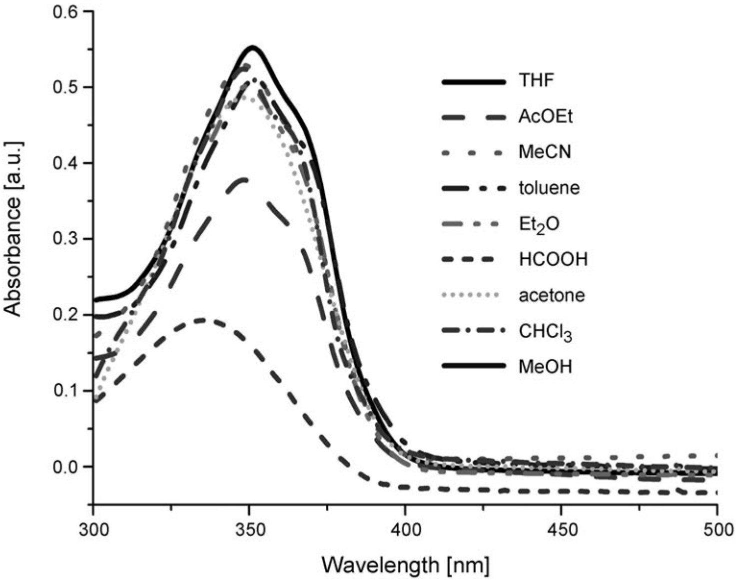


Fig. 3. *UV/VIS Absorption spectra of* **3d** *in various solvents* ($c = 10^{-5}$ M)

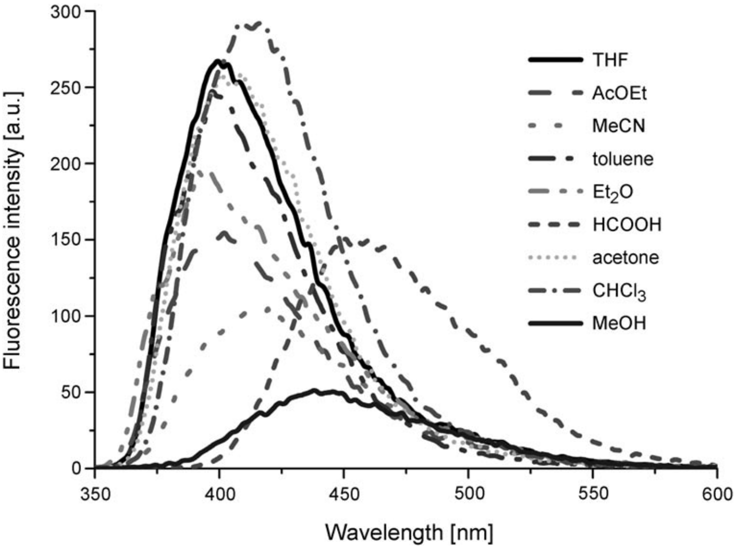


Fig. 4. *Fluorescence spectra of* **3d** *in various solutions* ($c = 10^{-5}$ M)

phenylene-linked bis-imidazoles [25]. This might be due to the steric hindrance. The disubstituted phenylene-linked bis-imidazoles can easier form H-bonds with solvents than the tetrasubstituted phenylene-linked bis-imidazoles.

Table 2. UV/VIS *Absorption and Fluorescence Properties of* **3d** *in Various Solvents* ($c = 10^{-5}$ M)

	ε [10^{-4} M^{-1} cm^{-1}]	$\lambda_{\max}^{\mathrm{Abs}}$ [nm]	$\lambda_{\max}^{\mathrm{Ex}}$ [nm]	$\lambda_{\max}^{\mathrm{Em}}$ [nm]	*Stokes* shift [nm]
Toluene	3.27	352	353	397	44
AcOEt	2.53	348	348.5	397	48.5
Et_2O	3.28	349	350	392.5	42.5
THF	3.67	351	351.5	399.5	48
Acetone	3.20	348	350	409.5	59.5
$CHCl_3$	3.15	348	354	411.5	57.5
MeCN	3.46	348	349	419.5	70.5
MeOH	3.18	351	350	438	88
HCO_2H	1.27	336	353	455.5	102.5

Conclusions. – In summary, a practical and effective microwave-assisted synthetic method under solvent-free conditions was successfully applied to the synthesis of the disubstituted phenylene-linked bis-imidazole derivatives **3a** – **3f** in 61.6 – 85.6% yields. The optical properties of **3a** – **3f** were investigated, showing that this series of disubstituted phenylene-linked bis-imidazole derivatives can serve as electron-transporting electro-luminescent materials, blue-light-emitting materials, and nonlinear optical materials.

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Experimental Part

General. All starting materials and solvents were obtained from commercial suppliers and used as obtained. Compounds **2a** [43], **2b** [44], **2c** [45], **2d** [46], **2e** [47], and **2f** [48] were prepared according to the published procedures. Microwave synthesis: *WBFY-201* apparatus. M.p.: *X-4* microscope electrothermal apparatus; uncorrected. UV and Fluorescence spectra: *HP-8453*-UV/VIS/near-IR spectrophotometer and *LS-55* spectrofluorometer, resp.; $\lambda_{\max}^{\mathrm{Abs}}$ (ε /10^4 M^{-1} cm^{-1}) and $\lambda_{\max}^{\mathrm{Em}}$ in nm; *Stokes* shift in nm; E_g^{Opt} in eV; optical pathlength of cells, 1 cm under all conditions; excitation wavelength $= \lambda_{\max}^{\mathrm{Em}}$ of the concerned compound. ^{1}H- and ^{13}C-NMR Spectra: *Bruker* spectrometer at 500 and 300 MHz, resp.; in $CDCl_3$ or (D_6)DMSO; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS: *Agilent 1100* LC/DAD/MSD; in *m*/*z*. Elemental analyses: *Vario-EL-III* elemental analyzer.

Benzene-1,4-dicarboximidamide Hydrochloride (1:2) (**1**). Benzene-1,4-dicarbonitrile (7.4 g, 58 mmol) was added in small portions over 30 min to a well-stirred soln. of $(Me_3Si)_2NLi$ in THF (240 ml, 240 mmol). The mixture was stirred at r.t. for another 3 h and then cooled to 0° in an ice bath. The reaction was quenched by careful addition of 6M HCl/EtOH (200 ml), and the mixture set aside for several hours. The precipitate was then filtered, washed with Et_2O, and recrystallized from EtOH/H_2O 1:1: **1** (10.4 g, 96%). White powder. M.p. > 300° ([49]: > 300°). ^{1}H-NMR ((D_6)DMSO, 300 MHz): 9.62 (*s*, 2 $^+NH_2=$); 8.37 (*s*, 2 NH_2); 8.03 (*s*, 4 arom. H).

2-Bromo-1-phenylethanone (**2a**). Yield 85.0%. White powder. M.p. 50 – 51° ([43]: 49 – 51°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.98 (*d*, $J = 4.4$, H–C(2′), H–C(6′)); 7.61 (*dd*, $J_1 = J_2 = 4.41$, H–C(4′)); 7.48 (*dd*, $J = 4.53$, 4.86, H–C(3′), H–C(5′)); 4.45 (*s*, CH_2Br).

2-Bromo-1-(4-methylphenyl)ethanone (**2b**). Yield 85.5%. White powder. M.p. 51 – 53° ([44]: 51 – 52°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.88 (*d*, $J = 5.0$, H–C(2′), H–C(6′)); 7.28 (*d*, $J = 4.8$, H–C(3′), H–C(5′)); 4.43 (*s*, CH_2Br); 2.43 (*s*, Me).

2-Bromo-1-(4-chlorophenyl)ethanone (**2c**). Yield 90.2%. White plates. M.p. 95 – 96° ([45]: 95 – 96°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.93 (*d*, $J = 5.1$, H–C(2′), H–C(6′)); 7.47 (*d*, $J = 5.2$, H–C(3′), H–C(5′)); 4.40 (*s*, CH_2Br).

2-Bromo-1-(thiophen-2-yl)ethanone (**2d**). Yield 88.0%. White plates. M.p. 31–33° ([46]: 33–35°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.71 (*m*, H–C(3′)); 7.62 (*m*, H–C(5′)); 7.17 (*m*, H–C(4′)); 4.37 (*s*, CH_2Br).

2-Bromo-1-(2,4-dimethylphenyl)ethanone (**2e**). Yield 80.0%. White plates. M.p. 41–42° ([47]: 41°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.60 (*d*, $J = 4.7$, H–C(2′)); 7.08 (*d*-like, 2 arom. H); 4.40 (*s*, CH_2Br); 2.51 (*s*, Me); 2.37 (*s*, Me).

2-Bromo-1-(4-methoxyphenyl)ethanone (**2f**). Yield 88.0%. White plates. M.p. 69–71° ([48]: 68–70°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.07 (*d*, $J = 5.4$, H–C(2′), H–C(6′)); 6.95 (*d*, $J = 5.4$, H–C(3′), H–C(5′)); 4.39 (*s*, CH_2Br); 3.89 (*s*, MeO).

Phenylene-Linked Bis-imidazole Derivatives **3**: *General Procedure.* Hydrochloride **1** (1.18 g, 5 mmol), 1-aryl-2-bromoethanone **2** (10–12 mmol), $KHCO_3$ (2 g, 20 mmol), and NaCl (5.85 g, 100 mmol) were thoroughly mixed in a mortar. The mixture was transferred into a beaker and irradiated with microwaves for 2 min (300 W). Then, the mixture was cooled to r.t. and irradiated for 2 min again. This procedure was repeated until the completion of the reaction (TLC (AcOEt)) monitoring. The crude product was washed with hot brine and recrystallized from MeOH/THF 1:1.

*2,2′-(1,4-Phenylene)bis[5-phenyl-1*H*-imidazole]* (**3a**): Yield 75.2%. White solid. M.p. 283–286° ([24]: 187–289°). ^{1}H-NMR ((D_6)DMSO, 300 MHz): 12.71 (br., 2 NH); 8.11 (*s*, 4 arom. H); 7.87 (*AA′* of *AA′BB′C*, $J = 7.1$, 4 arom. H); 7.79 (*s*, 2 arom. H); 7.39 (*BB′* of *AA′BB′C*, $J = 7.3$, 4 arom. H); 7.24 (*C* of *AA′BB′C*, $J = 7.5$, 2 arom. H). ^{13}C-NMR ((D_6)DMSO, 300 MHz): 145.6; 129.9; 128.9; 128.4; 127.9; 126.2; 125.1; 124.3. EI-MS: 363.2 ($[M+H]^+$, $C_{24}H_{18}N_4^+$; calc. 362.15). Anal. calc. for $C_{24}H_{18}N_4 \cdot 2\,H_2O$ (398.47): C 72.34, H 5.57, N 14.06; found: C 72.25, H 5.60, N 13.99.

*2,2′-(1,4-Phenylene)bis[5-(4-methylphenyl)-1*H*-imidazole]* (**3b**): Yield 70.4%. White solid. M.p. > 310°. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 12.64 (br., 2 NH); 8.10 (*s*, 4 arom. H); 7.76 (*AA′* of *AA′BB′*, $J = 7.10$, 4 arom. H); 7.68 (*s*, 2 arom. H); 7.21 (*BB′* of *AA′BB′*, $J = 6.9$, 4 arom. H); 2.33 (*s*, 2 Me). ^{13}C-NMR ((D_6)DMSO, 300 MHz): 145.5; 135.4; 129.9; 129.0; 125.1; 124.3; 114.0; 20.7. EI-MS: 391.2 ($[M+H]^+$, $C_{26}H_{22}N_4^+$; calc. 390.18), 389.1 ($[M-H]^+$), 779.0 ($[2M-H]^+$), 781.2 ($[2M+H]^+$). Anal. calc. for $C_{26}H_{22}N_4 \cdot 2\,H_2O$ (426.51): C 73.22, H 6.14, N 13.14; found: C 73.26, H 6.18, N 13.19.

*2,2′-(1,4-Phenylene)bis[5-(4-chlorophenyl)-1*H*-imidazole]* (**3c**): Yield 85.6%. White solid. M.p. > 310°. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 12.67 (br., 2 NH); 8.10 (*s*, 4 arom. H); 7.89 (*AA′* of *AA′BB′*, $J = 8.3$, 4 arom. H); 7.76 (*s*, 2 arom. H); 7.43 (*BB′* of *AA′BB′*, $J = 8.3$, 4 arom. H). ^{13}C-NMR ((D_6)DMSO, 300 MHz): 145.8; 133.5; 132.7; 130.5; 129.9; 128.5; 128.0; 126.0; 125.2; 124.5. EI-MS: 429.1 ($[M-H]^+$, $C_{24}H_{16}N_4Cl_2^+$, calc. 430.08). Anal. calc. for $C_{24}H_{16}Cl_2N_4 \cdot 2\,H_2O$ (467.35): C 61.68, H 4.31, N 11.99; found: C 61.59, H 4.27, N 12.12.

*2,2′-(1,4-Phenylene)bis[5-(thiophen-2-yl)-1*H*-imidazole]* (**3d**): Yield 61.6%. White solid. M.p. > 310°. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 12.77 (br., 2 NH); 8.04 (*s*, 4 arom. H); 7.68 (*s*, 2 H); 7.35 (*AB* of *ABC*, 4 arom. H); 7.06 (*C* of *ABC*, $J = 4.6$, 2 arom. H). ^{13}C-NMR ((D_6)DMSO, 300 MHz): 145.2; 138.5; 136.8; 129.7; 128.5; 127.6; 125.2; 124.6; 123.2; 121.4; 113.8. EI-MS: 373.1 ($[M-H]^+$, $C_{20}H_{14}N_4S_2^+$; calc. 374.07). Anal. calc. for $C_{20}H_{14}N_4S_2 \cdot 2\,H_2O$ (410.51): C 58.52, H 4.42, N 13.65; found: C 58.59, H 4.37, N 13.52.

*2,2′-(1,4-Phenylene)bis[5-(2,4-dimethylphenyl)-1*H*-imidazole]* (**3e**): Yield 65.6%. White solid. M.p. > 310°. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 12.64 (br., 2 NH); 8.10 (*s*, 4 arom. H); 7.73 (*s*, 2 arom. H); 7.38 (*s*, 2 arom. H); 7.07 (*BC* of *ABC*, 4 arom. H); 2.30 (*s*, 2 Me); 2.17 (*s*, 2 Me). ^{13}C-NMR ((D_6)DMSO, 300 MHz): 144.8; 135.4; 134.2; 131.3; 130.0; 128.0; 126.2; 125.1; 21.4; 20.6. EI-MS: 419.3 ($[M+H]^+$, $C_{28}H_{26}N_4^+$; calc. 418.22), 417.3 ($[M-H]^+$). Anal. calc. for $C_{28}H_{26}N_4 \cdot 2\,H_2O$ (454.56): C 73.98, H 6.65, N 12.33; found: C 73.79, H 6.57, N 12.48.

*2,2′-(1,4-Phenylene)bis[5-(4-methoxyphenyl)-1*H*-imidazole]* (**3f**): Yield 64.8%. White solid. M.p. > 310°. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 12.59 (br., 2 NH); 8.42 (*s*, 4 arom. H); 7.80 (*m*, 6 arom. H); 6.91 (*s*, 4 arom. H); 3.78 (*s*, 2 MeO). ^{13}C-NMR ((D_6)DMSO, 300 MHz): 158.0; 157.2; 145.3; 141.2; 130.0; 125.7; 125.1; 113.9; 113.2; 55.6. EI-MS: 423.2 ($[M+H]^+$, $C_{26}H_{22}N_4O_2^+$; calc. 422.17), 421.1 ($[M-H]^+$). Anal. calc. for $C_{26}H_{22}N_4O_2 \cdot 2\,H_2O$ (458.51): C 68.11, H 5.72, N 12.22; found: C 68.29, H 5.57, N 12.16.

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