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Mass spectrometry studies on *meso*-substituted corroles and their photochemical decomposition products

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Corroles, ring-contracted analogs of porphyrins, are an important class of compounds which have attracted the attention of many researchers in the fields of organic, coordination and physical chemistry. In the present work, the stability and the decomposition pathways of a diverse set of *meso*-substituted corroles have been studied using mass spectrometry (MS), UV–Vis absorption and preparative methods combined with NMR spectroscopy. Four different ionization methods (electrospray ionization, field desorption, atmospheric pressure photoionization and atmospheric pressure chemical ionization) were utilized to investigate light- and oxygen-induced decomposition in various solvents. It was found that the rate of decomposition in MeCN is significantly higher than in CH₂Cl₂, hexane, MeOH and ethyl acetate. HR-MS combined with CID–MS/MS enabled us to identify the products of initial decomposition. Surprisingly, numerous smaller open-chain compounds were also detected. Large-scale decomposition of a corrole bearing sterically hindered substituents at positions 5 and 15 allowed us to isolate mg quantities of three decomposition products: isocorrole and isomeric biliverdin-type species. These are formed as a result of oxygen attack on the *meso*-10 position. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: corroles; mass spectrometry; photochemistry; electrospray ionization; field desorption; photoionization

Introduction

Corroles, porphyrin analogs contracted by one carbon, emerged a few years ago as an independent area of research.^[1] Their coordination chemistry,^[2] photophysics,^[3] synthesis,^[4] chemical transformations,^[5] electrochemistry^[6] and other properties^[7] have recently been studied in great detail. One of the crucial factors governing the use of these molecules is their stability. Corroles have the same 18- π electron system as porphyrins but have one less atom in the core, which results in greater electron density. This in turn is responsible for their lower stability on exposure to oxygen in air. The lower stability of corroles versus porphyrins has been described in a number of papers^[8–16] and various decomposition products were identified: biliverdin,^[8–11,14,15] isocorroles^[13] and $\beta - \beta$ linked dimers and trimers.^[16] As expected, the oxygen stability of meso-substituted corroles increases when electronwithdrawing substituents are placed on the periphery of the macrocycle.^[17] This can be correlated with their first oxidation potential values.^[6a] Here we present the first comprehensive study on the stability and light-induced decomposition of corroles in solutions utilizing mass spectrometry (MS) as the primary analytical tool. The motivation to perform this study came from the several directions: (1) previous electrospray ionization (ESI)-MS data collected by us suggested the presence of additional signals in the samples of pure, freshly prepared corrole solutions, which we need to identify and characterize. We also need to investigate the potential of MS as a quick and reliable tool for examining the purity of corroles. (2) In-depth analysis of the literature reveals that various authors describe different decomposition products of rather similar corroles. This effect remains unexplained and there

is clearly a need for a comprehensive understanding on this topic. (3) The detailed data on the routes and rates of decomposition of corroles with diverse patterns of substituents in various solvents should be helpful in choosing the right pattern of substituents to perform further reactions with these molecules. MS is a very powerful and sensitive analytical method. However, the number of publications related to the analysis of corroles using MS techniques is limited.^[18-20] Obviously, there are many examples in the literature regarding the use of various MS ionization techniques [EI, ESI, FAB, field desorption (FD), MALDI]^[4,21] to confirm the molecular weight of prepared corroles. Additionally, MALDI-time of flight (TOF) has been used to monitor the conversion reaction of corrole to porphyrin.^[10] One of the aims of our study was to apply MS techniques to monitor processes that occur in solutions containing corroles. Four ionization techniques were used: FD, ESI, atmospheric pressure photoionization (APPI) and atmospheric pressure chemical ionization (APCI).

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Chart 1. The structures and nominal molecular masses of corroles studied.

Results and Discussion

Mass spectrometry studies in various solvents

As the stability of corroles strongly depends on the type of substituents located on the periphery of the macrocycle, we identified a diverse set of *meso*-substituted corroles bearing electron-withdrawing, electron-donating and sterically hindered substituents for our study (Chart 1). These compounds were synthesized according to the well-established literature procedures just before investigation.^[12,22,23]

The stability of corroles in the solution was tested in the following solvents: methanol (ESI, APPI), acetonitrile (ESI, APPI), ethyl acetate (APPI), dichloromethane (FD) and hexane (APCI, APPI). In all cases, corroles were dissolved in a drop of CH₂Cl₂ and diluted with the appropriate non-degassed solvent. Samples were kept at ambient light in contact with air. Mass spectra were recorded immediately after the dilution, after 30 min and after 1 h (sometimes also after a longer period of time). All experiments showed that the mass spectra of the corrole solutions change over time. The intensity of additional peaks corresponding to decomposition products increased continuously with time. The decomposition of corroles was the most rapid in acetonitrile. We observed slower decomposition in methanol and ethyl acetate. In CH₂Cl₂ and hexane, corroles were relatively stable. Typical changes that were observed in the mass spectra of corrole solutions are presented in Fig. 1. APCI was used because ESI does not have a possibility to measure spectra in hexane and ethyl acetate. The spectra in methanol, hexane and ethyl acetate recorded after 1 h show additional peaks of lower intensity in comparison with the spectrum in acetonitrile recorded after 5 min. The correlation of the rate of corrole decomposition and oxygen solubility in the solvents used was investigated (Table S2, Supporting Information). Surprisingly, we found that the stability of corroles in solvents which contain the highest amount of oxygen is rather high, whereas CH_3CN does not dissolve molecular oxygen particularly well.

The intriguing results obtained for acetonitrile solutions led us to focus on this solvent for further experiments. It was found that all six corroles undergo oxidation but at different rates and to different extents. Our study showed that corrole **6** was clearly the most stable. This can be attributed to the electron-withdrawing effect of the pentafluorophenyl group in the *meso*-positions. The relative stability of corroles in MeCN can be estimated on the basis of the ratio of isocorrole and biliverdin *versus* corrole over time. Based on relative intensities of peaks corresponding to a corrole and its oxidation products as a function of time, the rank of stability is: $6 > 3 > 1 \sim 2 > 4 \sim 5$. In the case of corrole **2**, the isocorrole formed is rapidly decomposed.

The results obtained by ESI, APCI and APPI ionization techniques show some important differences (Fig. 2). Spectra acquired using APCI and APPI methods differ only slightly in the relative peak intensities which can be attributed to the different ionization efficiencies of these methods for molecules with different structural features. In the ESI spectrum, however, an additional $[M + 15]^+$ peak appears while the intensity of the $[M + 17]^+$ peak is quite low. Additionally, the relative intensity of the $[M + H]^+$ peak is much higher compared to the APCI and APPI spectra. This may reflect the higher ability of milder ESI ionization to generate stable $[M + H]^+$ ions compared to APCI and APPI methods which prefer the formation of M^{+•} ions due to the higher energy transfer during the ionization process.

Besides the $M^{+\bullet}$ molecular ion and the protonated molecule $([M + H]^+$ ion), additional ions are observed in the spectra of all corroles: $[M - 1]^+$, $[M + 15]^+$ (usually observed in ESI-MS spectra), $[M + 17]^+$, $[M + 33]^+$ and rarely $[M + 49]^+$.

As expected, the $[M - 1]^+$ ion corresponds to $[M - H]^+$ species. We observed $[M - H]^+$ ion in spectra recorded using all ionization techniques and its abundance did not increase during





Figure 1. Light-induced decomposition of corrole 1 (M = 635 Da) in various solvents studied by APCI-MS. The [M + 15]⁺, [M + 17]⁺ and [M + 33]⁺ ions were assigned to [M - H + 0]⁺, [M + 0 + H]⁺ and [M + 20 + H]⁺ species, respectively. See text for more details.

measurement. In the spectra recorded for methanolic solution, $[M - H]^+$ ion was present at very low intensity or was not observed at all (Fig. 1). The addition of triethylamine to the acetonitrile solutions of corroles **1**, **3** and **4** led to an increase in the abundance of $[M - H]^+$ ion (FD ionization). This ion was most likely formed from the radical cation of corrole by the loss of a hydrogen atom during the ionization. Alternatively, it can be formed by the anodic two-electron oxidation of the $[M - H]^-$ anion on the surface of the ESI capillary (Scheme 1).

The $[M + 15]^+$ and $[M + 17]^+$ ions were assigned to $[M - H + O]^+$ and $[M + O + H]^+$ species, respectively. The presence of both ions is related to the oxidation of corrole. Therefore, the $[M + O + H]^+$ ion corresponds to the protonated [M + O] molecule with the

structure of isocorrole (formula **7** in Scheme 2). This assignment was confirmed by HR-MS and in the preparative decomposition experiment with corrole **1** (*vide infra*). The $[M - H + O]^+$ ion is observed mainly in ESI ionization and is most likely the oxidized $[M - H]^+$ ion. The origin of the $[M + 33]^+$ ion can be explained by the addition of two oxygen atoms and a proton to the molecule of corrole: $[M + 2O + H]^+$. The presence of this ion suggests that biliverdin-like species are formed in the oxidation process. This assumption has been supported by MS/MS experiments of the $[M + 2O + H]^+$ ions (Fig. 3). The presence of the biliverdin-like species was further confirmed in the preparative decomposition experiment with corrole **1** (described below). A comparison of various techniques clearly shows that FD is the method of choice



Figure 2. ESI, APCI, APPI and FD mass spectra of compound **3** in acetonitrile recorded 30 min after the preparation of the solution. The $[M + 15]^+$, $[M + 17]^+$ and $[M + 33]^+$ ions were assigned to $[M - H + 0]^+$, $[M + 0 + H]^+$ and $[M + 20 + H]^+$ species, respectively. See text for more details.

for studying corrole decomposition as it reveals all impurities present but does not induce any reactions in the spectrometer. In contrast, corrole oxidation in the ion-source during ESI-MS can lead to the wrong conclusion about corrole purity: [M + 15] and [M + 17] peaks are always present.

In order to establish the structures of the oxidation products, we performed a number of MS/MS experiments (Figs 3 and S6, Supporting Information). The results show that for *trans*-A₂B corroles, it is possible to determine which isomers with the mass [M + 16] and [M + 32] are formed in the oxidation process. Even if the acylium cation of an appropriate aldehyde is difficult to detect or observe, it is possible to observe an elimination of a neutral molecule or the respective radical in the product spectra. On the basis of these results, it is possible to determine the position of the hydroxyl group in the molecule of isocorrole [M + O] and, consequently, in which position the macrocyclic ring has opened. For obvious reasons, the determination of the side of the ring-opening is impossible for A₃-corroles.

$$M_{in \ solution} \xrightarrow{-e} M^{+} \xrightarrow{-H^{+}} [M - H]^{+}$$
$$M_{in \ solution} \xrightarrow{-H^{+}} [M - H]^{-} \xrightarrow{-2e} [M - H]^{+}$$

Scheme 1. Possible mechanisms of $[M - H]^+$ formation in ion sources.

The lack of sterically hindered substituents at *meso*-positions results in oxidative attack both at positions 5 and 10 (Figs 3(c) and

S6(c), Supporting Information). This is in line with the oxidation product observed by Paolesse *et al.*^[13] with DDQ in MeOH of 5,10,15-tris(*p*-tolyl)corrole. The next oxidation product observed is the [M + 30] compound. The presence of an [M + 30] compound was also observed in our preparative decomposition experiment with corrole **1** (described below). In ESI and APCI ionization techniques, it appears as the protonated ion [M + 30 + H]⁺, but in FD as a radical cation [M + 30]^{+•}. Both signals appeared after a longer reaction time in MeCN but their abundances were always low.

In the course of our research, we noticed more signals related to oxidation processes. During APCI experiments we observed additional ions with m/z lower than the molecular ion. Figure 4(a) and (b) shows APCI mass spectra of corrole **2** and possible structures of the oxidation product observed at m/z 569 in positive mode and at m/z 567 in negative mode. We acquired the product ion spectrum of the m/z 569 and on the basis of this we were able to determine a possible structure of the oxidation product (Fig. 5). This is the most probable structure based on the presence of m/z 439 and 309 peaks in the product ion spectrum. A similar oxidation product was observed in the preparative decomposition experiment with corrole **1** (*vide infra*). Additionally, we observed that corroles and their oxidation products in negative mode ionized very abundantly. Spectra recorded in negative mode were similar to those in positive ion mode and contain analogous signals.

It was observed that the oxidation process does not take place in the absence of light even if oxygen is present. Similarly, when we add formic acid to the sample, we did not observe additional



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Figure 3. CID spectra of the $[M + 2O + H]^+$ ions of corroles 4(a), 1(b), 5(c) and 6(d) in MeCN.

signals in the mass spectra of corroles. These results clearly show that the presence of an acid as well as the absence of light inhibits the oxidation of the studied compounds. Interesting results were obtained after triethylamine addition. Under such conditions, the [M + 32] product was formed in small amounts.

Synthetic and UV-Vis studies

In order to fully characterize the oxidation products observed, we carried out the preparative scale decomposition of one corrole. The aim was to isolate and elucidate the structures of the compounds observed in MS. The electron-rich corrole **1** was selected for the preparative scale decomposition reaction. Based on MS experiments, acetonitrile was selected as the solvent to provide the most rapid decomposition. A sample of **1** was dissolved in acetonitrile and exposed to sunlight for

60 h. TLC analysis revealed that after this time corrole **1** had decomposed almost completely into a number of products, of which only three were isolated in sufficient amounts. Compounds **7**, **8** and **9** were purified and characterized by NMR (1D and 2D experiments, Figs S7–S18, Supporting Information), MS and UV–Vis spectra (Fig. S5, Supporting Information). Compound **7** was relatively stable, although it decomposed partially into a navy blue compound during chromatography, significantly in methylene chloride/hexane. In contrast, compounds **8** and **9** turned out to be stable for at least 15 h in the chloroform solution used for NMR analysis. Additionally, the fractions containing compounds formed in trace amounts were analyzed with the use of MS (Table S1, Supporting Information).

Among the three decomposition products, isocorrole **7** was the easiest to identify. Its structure was fully confirmed by NMR



0 (2070)

Scheme 2. Proposed structures for the main products of the photochemical oxidation of corrole **1**.

and comparison with Paolesse's compounds.^[13,15] The remaining two products were more difficult to identify. HR-MS revealed that they have the same molecular masses which correspond to the open-chain ketones depicted in Scheme 2. Detailed NMR analysis showed that in both compounds the decomposition site is the carbon-carbon bond in the *meso*-10 position. The identical CID mass spectra suggest that these compounds differ only slightly and are most likely geometrical isomers. A shifted NH proton signal for **9** eventually allowed us to identify it as an open-chain ketone with



Figure 4. Positive (a) and negative (b) APCI spectra of compound **2** in MeCN recorded 30 min after the preparation of the solution.

a tilted pyrrole ring (E/Z isomers). This assignment is supported by DFT calculations of NMR spectra (Figs S19–S21, Supporting Information). Such compounds have not been reported in the literature up to now. The most characteristic feature of their absorption spectrum is a strong signal at 555 nm. Both **8** and **9** form complexes with Zn^{2+} , whereby the complex with **8** is distinctly green in solution.

Our results strongly suggest that the position of the initial attack of oxygen on the corrole core is governed by both electronic and steric factors. According to Paolesse, the chemical oxidation of a *meso*-substituted corrole possessing both electron-withdrawing and sterically hindered groups in the *meso*-position does not occur, whereas in the case of unhindered ones, oxidation occurs at position $5.^{[13-15]}$ Our ketone is regioisomeric to that which Paolesse reported to be formed during chemical oxidation of triaryl corroles.^[13-15] Surprisingly, the A₂B-porphyrin observed by Guilard *et al*.^[10] for structurally similar 5,15-bismesityl-10-(4-nitrophenyl)corrole was neither observed by MS nor via isolation of the products in our experiments.

The stability of a solution of corrole **1** was studied using UV spectrophotometry. Measurements were performed both in CH_3CN and CH_2Cl_2 in the presence and absence of light (Figs S1-S4, Supporting Information). No changes were observed in the absence of light. On the other hand, in the presence of light, the intensity of the Soret band quickly decreased and the formation of a broadband around 550 nm, corresponding to the formation of ketones **8** and **9**, was observed. These spectroscopic



Figure 5. Product ion spectrum of m/z 569 ion of one of the products resulting from the oxidative decomposition of corrole 2.

studies confirm that the decomposition in the presence of light is faster in CH_3CN than in CH_2Cl_2 . The origin of this phenomenon is unclear at this point.

Summary and Conclusions

The following conclusions can be drawn: (1) MS was found to be useful not only in the analysis of the purity of corroles but also in the detection and structure determination of the oxidative decomposition products of corroles. (2) FD is the most suitable ionization method to evaluate the purity of corroles. (3) Electrospray induces oxidation that results in the detection of the [M + 15] signal (isocorrole), even if a corrole sample is pure. (4) The rate of light and oxygen-induced decomposition decreases when the corrole possesses electron-withdrawing substituents. (5) Decomposition of corroles bearing sterically hindered substituents at positions 5 and 15 leads to attack at position 10 and results in the formation of isocorrole and ketones in substantial yield as well as more than 15 other open-chain products.

Experimental Section

General methods

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH₂Cl₂, hexane, ethyl acetate) were distilled prior to use. All reported ¹H NMR and ¹³C NMR spectra were recorded using a Varian VNMRS 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; J values are given in Hz. The UV-Vis absorption spectra were recorded in CH₂Cl₂. The absorption wavelengths are reported in nm with the extinction coefficient in M^{-1} cm⁻¹ in brackets. Melting points were determined using a Boetius-type apparatus. Chromatography was performed on silica (200-400 mesh) or alumina. Dry column vacuum chromatography (DCVC) was performed on preparative thin-layer chromatography silica. Mass spectra were recorded using ESI, APCI, APPI and FD ionization methods. ESI, APCI and APPI mass spectra were recorded on 4000 QTrap triple guadrupole/linear ion trap mass spectrometer (Applied Biosystems) and FD spectra were recorded on GCT Premier high resolution TOF mass spectrometer (Waters/Micromass). The IR spectra were recorded in the film and the wavenumbers are expressed in cm^{-1} . Corroles **1(a-f)** were prepared according to the literature procedures.^[12,22,23]

Corrole **1** (160 mg, 0.25 mmol) was dissolved in MeCN (1000 ml) and the solution was exposed to sunlight for 60 h. Subsequently, the reaction mixture was evaporated to the dryness and the resulting solid was preliminarily chromatographed (DCVC, silica gel, hexanes/ethyl acetate 19:1 to 4:1, then hexanes/acetone 4:1, then acetone, then MeOH) to afford several contaminated products of decomposition. Fractions containing compounds formed in trace amounts were analyzed with the use of MS. The rest were submitted to further purification.

Chromatography of the first main fraction (DCVC, silica gel, hexanes/acetone 97:3) followed by the second chromatography (DCVC, silica gel, hexanes/methylene chloride 3:2) furnished compound **7** (13 mg, 8%), which was then suspended in hexanes and filtered to afford green crystals.

 $R_{\rm f}$ = 0.43 (silica gel, acetone/hexane, 1:3); m.p. >330 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 2.12 (s, 6H, CH₃), 2.15 (s, 6H, CH₃), 2.34 (s, 6H, CH₃), 2.84 (s, 1H, OH), 6.30 (d, J(H,H) = 4.3 Hz, 2H, β-H), 6.34 (d, J(H,H) = 4.3 Hz, 2H, β-H), 6.61 (d, J(H,H) = 4.1 Hz, 2H, β-H), 6.92 (s, 4H, mesityl), 7.55 (m, AA' part of the AA'XX' system, 2H, NC-C₆H₄), 7.83 (m, AA' part of the AA'XX' system, 2H, NC-C₆H₄), 7.83 (m, AA' part of the AA'XX' system, 2H, NC-C₆H₄), 15.5 ppm (bs, 2H, NH); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 20.0, 20.1, 21.1, 74.9, 111.1, 116.2, 117.4, 118.8, 126.8, 127.8, 127.9, 128.0, 128.1, 132.2, 132.4, 136.5, 136.9, 137.8, 140.6, 140.8, 141.4, 146.4, 147.0, 162.2 ppm; IR (film): ν bar = 808, 824, 1033, 1353, 1559, 1603, 1739, 2229 (CN), 2923, 3193 (N-H), 3433 cm⁻¹ (O-H); UV-Vis (CH₂Cl₂): λ (ε) = 428 (31 600), 348 (11 400), 666 nm (4200 M⁻¹ cm⁻¹); HRMS (FD): *m/z* calcd. for C₄₄H₃₇N₅O: 651.2998; found: 651.2990, isotope profiles match.

The next fraction, consisting of two isomeric compounds **8** and **9**, was submitted to chromatography (DCVC, silica gel, hexane/ethyl acetate 93:7 to 3:1) followed by three consecutive chromatographies (DCVC, silica gel, hexanes/acetone 23:2 to 4:1), which provided the contaminated compound **8**, and the chromatographically pure compound **9** (47 mg, 28%). Two subsequent chromatographies of the product **8** (DCVC, silica gel, hexanes/acetone 23:2 to 9:1) furnished the pure isomer **8** (85 mg, 51%). Both compounds were suspended in hexane and filtered to afford navy blue crystals, which were submitted to analyses.

Compound **8**: $R_f = 0.56$ (silica gel, ethyl acetate/hexanes, 3:2), 0.48 (silica gel, acetone/hexanes, 2:3); m.p. 201.3–203.7 $^{\circ}$ C; ¹H NMR (600 MHz, CDCl₃, 25 $^{\circ}$ C, TMS): δ = 2.08 (s, 6H, CH₃), 2.12 (s, 6H, CH₃), 2.20 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 6.02 (d, J(H,H) = 4.1 Hz, 1H, β -H), 6.05 (d, J(H,H) = 5.5 Hz, 1H, β -H), 6.52 (m, 1H, β -H), 6.57 (d, J(H,H) = 5.5 Hz, 1H, β -H), 6.61 (d, J(H,H) = 4.1 Hz, 1H, β -H), 6.68 (d, J(H,H) = 4.7 Hz, 1H, β -H), 6.94 (s, 2H, mesityl), 6.96 (d, $J(H,H) = 4.7, 1H, \beta$ -H), 6.97 (s, 2H, mesityl), 6.98 (d, $J(H,H) \cong 4.2$ Hz, 1H, β -H), 7.75 (d, J(H,H) = 8.1 Hz, 2H, NC-C₆H₄), 7.98 (d, J(H,H) = 8.1 Hz, 2H, NC-C₆H₄), 9.0 ppm (bs, 3H, NH); ¹³C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 20.0, 20.1, 21.10, 21.13, 115.1, 116.3, 117.3, 115.1, 116.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 117.3, 115.1, 116.3, 115.1, 116.3, 117.3, 115.1, 116.3, 116$ 117.8, 118.2, 119.6, 122.9, 126.4, 128.1, 128.9, 129.3, 130.6, 131.5, 132.2, 132.7, 132.8, 134.4, 134.5, 134.7, 135.8, 137.0, 137.4, 137.8, 137.9, 138.1, 138.2, 142.1, 154.3, 160.9, 173.1 and 182.0 ppm; IR (film): ν bar = 804, 1285, 1603, 1681, 2230 (CN), 2919, 3264 cm⁻¹ (N-H); UV-Vis (CH_2CI_2) : λ (ε) = 396 (36 800), 557 (26 800), 757 nm (400 M⁻¹ cm⁻¹); HRMS (FD): *m/z* calcd. for C₄₄H₃₇N₅O₂: 667.2947; found: 667.2953, isotope profiles match.

Compound **9**: $R_f = 0.49$ (silica gel, ethyl acetate/hexanes, 3:2), 0.42 (silica gel, acetone/hexanes 2:3); m.p. 127.5-128.3 °C; ¹H NMR (600 MHz, CDCl₃, 25 $^{\circ}$ C, TMS): δ = 2.10 (s, 6H, CH₃), 2.15 (s, 6H, CH₃), 2.27 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 6.08 (d, *J*(H,H) = 4.1 Hz, 1H, β -H), 6.24 (d, J(H,H) = 4.0 Hz, 1H, β -H), 6.52 (dd, J(H,H) = 5.8 Hz, 1.9 Hz, 1H, β -H), 6.70 (3H, three overlapping signals of two β -H and one amide NH), 6.84 (d, J(H,H) = 4.0 Hz, 1H, β -H), 6.90 (d, J(H,H) = 4.7 Hz, 1H, β -H), 6.96 (s, 2H, mesityl), 6.99 (s, 2H, mesityl), 7.83 (m, AA' part of the AA'XX' system, 2H, NC-C₆H₄), 8.02 (m, AA' part of the AA'XX' system, 2H, NC-C₆H₄), 8.08 ppm (dd, J(H,H) = 5.8 Hz, 1.9 Hz, 1H, β -H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta = 19.6, 20.1, 21.1, 21.2, 115.3, 115.9, 116.7, 117.2, 117.9, 118.1,$ 119.8, 124.8, 126.1, 126.4, 128.1, 129.2, 129.3, 130.7, 131.2, 132.4, 132.6, 132.7, 134.3, 134.5, 134.6, 135.0, 136.1, 136.8, 137.0, 138.0, 138.5, 138.7, 142.0, 154.3, 160.9, 170.4 and 182.2 ppm; IR (film): v bar = 805, 1283, 1604, 1686, 2230 (CN), 2923, 3239 and 3440 cm⁻¹; UV–Vis (CH₂Cl₂): λ (ε) = 398 (36 900), 565 nm (17 900 M⁻¹ cm⁻¹); HRMS (FD): *m/z* calcd. for C₄₄H₃₇N₅O₂: 667.2947; found: 667.2921, isotope profiles match.

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Supporting information

Supporting information may be found in the online version of this article.

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