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Quinoidal alkali imidate salts: Dipotassium pyrazine-2,5-bis(olates), a novel class of quinoidal piperazine-2,5-dione derivatives

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This article is dedicated to Professor Hans-Günther (Hagga) Schmalz, on the occasion of his retirement, his contribution to organometallic-mediated organic synthesis and his positive impact on the chemists of developing nations

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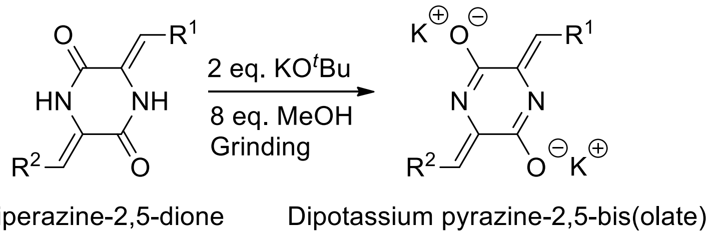
Abstract

Piperazine-2,5-diones are common structural motifs in biologically active natural products. However, in recent years, applying conjugated piperazine-2,5-dione derivatives, for example, the *p*-azaquinodimethanes, in organic semiconductors and singlet fission polymers has sparked a renewed interest in these compounds. A range of thirteen piperazine-2,5-diones was synthesised with various donor and acceptor groups. These compounds were subsequently converted to their dipotassium pyrazine-2,5-bis(olate) derivatives, utilising a solvent-assisted mechanochemical preparation method. This is one of the first reported cases, detailing a series of isolated quinoidal alkali imidate salts. All dipotassium pyrazine-2,5-bis(olates) were characterised using ATR-FTIR, high-resolution MS, and NMR spectroscopy.



Keywords: Pyrazine-2,5-bis(olate), piperazine-2,5-dione, potassium imidate salt, imidic acid salt

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Introduction

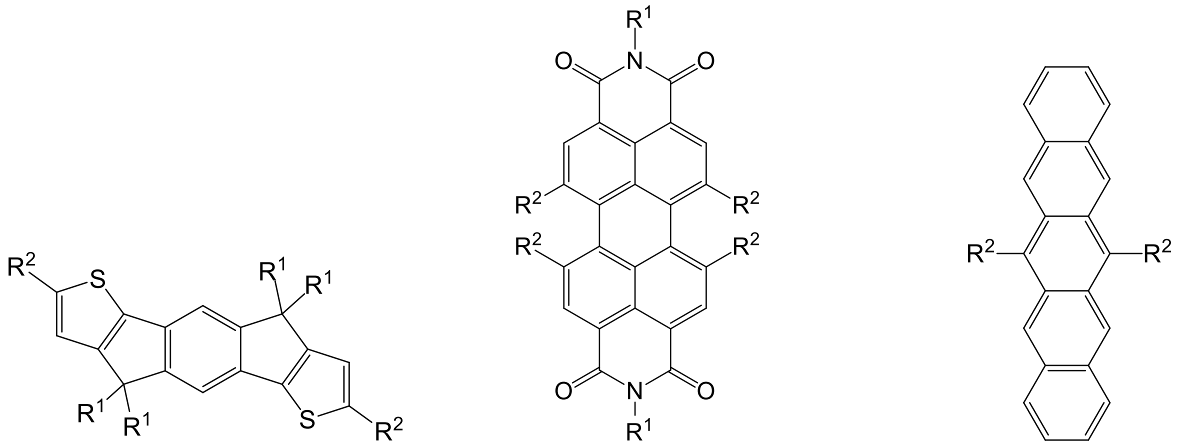
The continuous innovation in the discipline of organic semiconductors has changed modern material science, particularly in areas like photovoltaics, flexible electronics, and thin-film transistors.[1] Among the potentially organic semiconducting motifs, some molecules such as (pent-)acenes have consistently outperformed others due to their electronic performance, processability, and stability. [2, 3] Over time, two groups of aromatic small-molecule semiconductors, perylenediimides and indacenodithiophenes, have become benchmarks for semiconductor performance (Figure 1a).[4] However, the continuous development of these structural motifs has reached a plateau and is, therefore, not actively pursued anymore.

Instead, research has shifted focus to other potential semiconductor moieties, such as quinoidal frameworks (Figure 1b), which also offer unique electronic properties. These unique properties include concentration-dependent colour adjustment and particle size control, by variation of perylene/cyanoanthracene ratios.[5] Another advantage of quinoidal structures is the ability to tune the HOMO-LUMO band gap, by synthetic modification of the structures, towards more efficient, narrower gaps. [4, 6, 7] The quinoidal molecules are also generally less heat- and light-sensitive compared to commonly studied fullerenes, therefore demonstrating improved longer-term efficiency.[8] Quinoidals can thus be employed as novel scaffolds that balance high charge mobility with oxidative and thermal stability.[9]

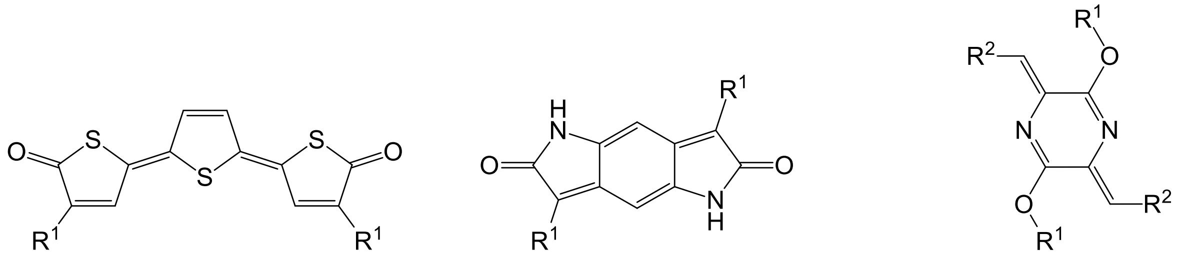
Quinoidal motifs have received comparatively less attention than other known aromatic semiconductors.[7, 9] However, quinoidal compounds often outperform the known compounds regarding the charge transport properties.[7, 10] Quinoidal semiconductors are also synthesised according to the donor-acceptor strategy.[9, 11, 12] Examples of some stable, commonly utilised quinoidal motifs include terthiophenediones, benzodipyrolediones and *p*-azaquinodimethanes, are depicted in Figure 1b.

The value of the quinoidal semiconductors becomes apparent when considering two widely applicable methods to improve semiconduction by synthetic modification namely, the development of more efficient donor-acceptor molecules, or the development of quinoidal moieties that are used as substituents in known semiconductor molecules. Both approaches can also be combined.[7, 9, 10, 14-16] However, the development of ambiently stable quinoidal moieties is challenging and has lagged the development of non-quinoidal moieties.

Piperazine-2,5-diones (**1**), Figure 2, are a class of biologically active cyclic dipeptides that are present in numerous food and beverage items. The quinoidal derivatives of **1** possess comparatively better stability than other quinoidal semiconductors. [17-21] The utility of this class of molecules extends beyond their biological applications. Certain hemipiperazines proved to be highly stable photo-switches. Some dialkoxy-modified *p*-azaquinodimethane derivatives, **7**, Scheme 1, have been utilised in the development of quinoidal semiconducting polymers, and singlet-fission polymers.[12, 22-25] By forming the *p*-azaquinodimethane moiety, the piperazine-2,5-dione core becomes stabilized in a quinoidal structure. The *p*-azaquinodimethane motif, **7**, is valued especially in organic semiconduction due to its ability to narrow the charge transfer band gap.[7, 11, 26]



a. Indacenodithiophene (p-type) Perylenediimide (n-type) Pentacene (p-type)



b. Terthiophenedione (mixed p/n-type) Benzodipyrroledione (n-type) *p*-Azaquinodimethane (p-type)

Figure 1. a. Examples of aromatic motifs encountered in organic semiconductors, **b.** Examples of quinoidal motifs encountered in organic semiconductors.[2-9, 13] R^1 and R^2 are generally aliphatic or aromatic substituents, respectively.

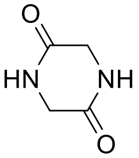


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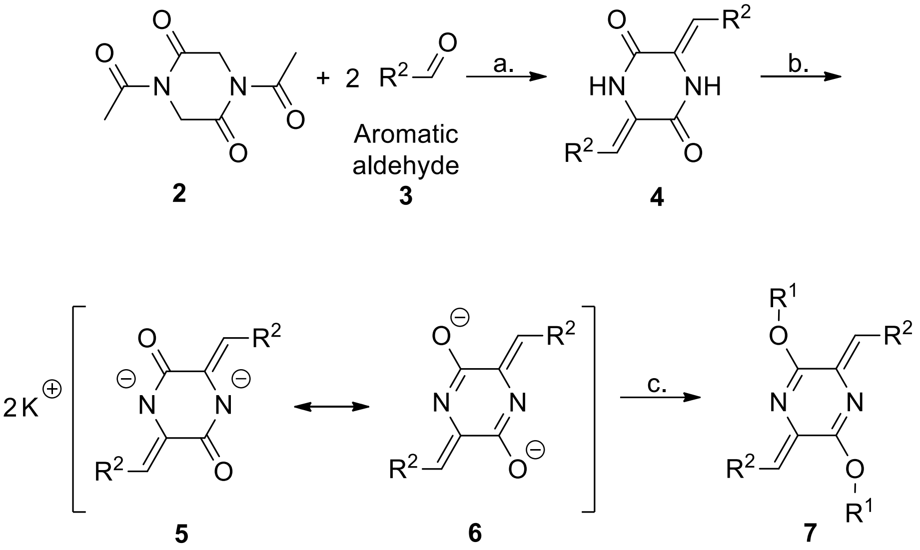
Figure 2. Piperazine-2,5-dione (**1**), is a valued functional group in pharmaceutical research, food products, and the development of quinoidal organic semiconductors.

The application of these quinoidal molecules to produce semiconductor materials is, however, hampered by solubility issues, especially in water. It is hypothesised that the alkali imidate derivatives of conjugated piperazine-2,5-diones, i.e. the dipotassium pyrazine-2,5-bis(olates) **6**, Scheme 1, form *in situ* during the synthesis of the *p*-azaquinodimethanes **7**, Scheme 1.[24] These salts improve the water-solubility of these compounds, which would improve their processability to a significant extent. The highly conjugated piperazine-2,5-diones **4**, Scheme 1, enable charge stabilisation over the nitrogen, carbon, and oxygen atoms in the functional group after deprotonation of the nitrogen by a strong base; similar to that commonly encountered in conjugated enolates, which facilitates salt formation.[12, 24, 25, 27]



Scheme 1. Synthesis route of p-azaquinodimethanes, **7**, from 1,4-diacetylpiperazine-2,5-dione, **2**, published by Liu, et. al.24 **a**. TEA, DMF, N2, 120 °C, overnight. **b**. K2CO3, DMF. **c**. bromoalkane, N2, 100 °C, 2 h.

In 2017, Liu *et al.* reported that **7** could function as ambiently stable building blocks for polymeric semiconductors.[24] Attempts to alkylate the nitrogen atoms of the conjugated precursor **4**, with haloalkanes in basic media, unfortunately, produced O-alkylated **7** in yields between 50–60% instead of the desired *N*-alkylated derivatives.

It was hypothesised that the nitrogen atoms of the conjugated piperazine-2,5-diones underwent deprotonation, with subsequent charge delocalisation and stabilisation over the amidic nitrogen, carbon, and oxygen, delivering intermediates **5** and **6** in Scheme 1. Due to the greater electronegativity of the oxygen over that of the nitrogen, preferential formation of the derivatives of **6**, i.e. the dipotassium imidate salts, occurs *in situ*.[24] Following these findings, numerous articles have been published regarding the *p*-azaquinodimethanes and their salt-forming properties.[11, 12, 25, 28, 29] At the time of writing, no work has been published on the isolation and purification of the alkali metal pyrazine-2,5-bis(olate) derivatives, presumably since metal imidate salts have only been expected to exist in solution.[30-32]

Even though Fytas *et al*. reported the isolation of potassium imidate salts in 2008, upon closer inspection of their work, their conclusions regarding the type of salt that formed were found to be incorrect.[33] The authors isolated the potassium imide salts of the piperazine-2,6-diones and not potassium imidate salts, as have been isolated in this work.[33] This is an important distinction, as the formation of quinoidal derivatives from conjugated piperazine-2,5-diones, explicitly requires the resulting compound to possess a ketimine double bond to ensure efficient charge transport as exemplified by **6** and **7** in Scheme 1. Based on this requirement, **6**, is expected to share the quinoidal character of **7**. Consequently, when considering the available literature, a lack of research regarding both the isolation of the dipotassium pyrazine-2,5-bis(olates) as well as the isolation of alkali imidate salts in general, exists. Valuable features of our synthesis approach to obtain **6**, lie in the circumvention of the usage of halogenated alkanes, relatively toxic solvents, and excess base to prepare a quinoidal motif from the conjugated form of **4**. Subsequently, a more sustainable route toward quinoidal semiconductors could be established.[24]

Consequently, this implies that **6** may possess comparable semiconducting properties to **7** due to their quinoidal nature whilst utilising relatively mild conditions to efficiently produce higher yields.[24] Compound **6** may also provide improved solubility over their uncharged counterparts in more environmentally benign solvents such as DMSO and aliphatic alcohols, positively impacting the large-scale manufacturing of electronic devices.[34] Based on their ionic nature, **6** the quinoidal salts also possess the potential to act as mixed ionic-electronic conductors, an important class of compounds in bioelectronics and organic electronic device manufacture.[35]

The mechanochemical synthesis method also utilises less energy, as the products are obtained after approximately 30 min of heating at 80 °C, under vacuum, compared to the **7** that are only obtained after 2 h of heating, at 100 °C, and that still need to be isolated and purified afterwards, employing column chromatography.[24]

Virtually no literature has been reported regarding the preparation and isolation of dipotassium pyrazine-2,5-bis(olates), i.e., the alkali imidate salts of conjugated piperazine-2,5-diones, **6**. Given the popularity of the corresponding *p*-azaquinodimethane derivatives in current organic semiconductor research, this absence is surprising.[11, 12, 24, 25, 28, 29] The traditional challenge associated with isolating stable imidic acid salts may explain this gap. Although the compound likely exists as a mesomer, it is generally accepted that the amide anion form (exemplified by intermediate **5** in Scheme 1) is favoured over the imidate ion form, **6**.[30, 31, 36] This assumption was originally shared by Liu *et al*. during their pioneering 2017 study. [24] However, as noted by Nakamura and co-workers, this preference is not universal and depends strongly on the nature of the conjugated system. [36]

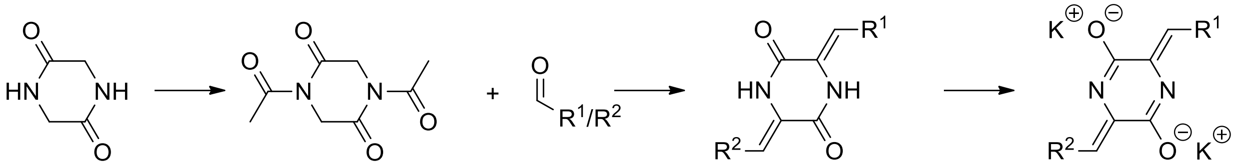
In this study, we demonstrate that the preparation, and isolation of potassium imidate derivatives of conjugated piperazine-2,5-diones, is both feasible and straightforward. The formation of the dipotassium pyrazine-2,5-bis(olates) (**6a**–**6m**) occurred irrespective of the nature of the conjugated substituents. While solvent-free methods were effective, the use of methanol ensured homogeneity of the final product. KO^{t}Bu was chosen as the base to facilitate the removal of by-products and ensure cleaner isolation. The study suggests a new, practical route to quinoidal salt production that can potentially be used to produce organic semiconducting scaffolds and mixed ionic-electronic conducting materials.

Results and Discussion

The following section outlines the synthesis, isolation, and characterisation of a unique series of thirteen dipotassium pyrazine-2,5-bis(olates) synthesized from both symmetrical and unsymmetrical conjugated piperazine-2,5-diones. A presentation of the main synthetic observations, yields, purities, spectroscopic analysis and an assessment of the physical properties is also reported. Additionally, special attention to the structural characteristics, solubility profiles, and spectral signatures of the desired quinoidal imidate salts are given.

The synthesis of 1,4-diacetylpiperazine-2,5-dione (**2**, Scheme 2) was straightforward, with the desired product isolated in quantitative yields and high purity, >99% based on ^{1}H NMR. It is of value to note that the mass of **2** could not be determined with HR-MS, even though ^{1}H and ^{13}C NMR results proved that the desired compound was present and pure. The mass spectrum obtained corresponds to those of piperazine-2,5-dione, 1-acetylpiperazine-2,5-dione and that of an unidentified 1-acetylpiperazine-2,5-dione dimer or an *N*-acetyl glycine tripeptide derivative. Formation of the piperazine-2,5-dione and 1-acetylpiperazine-2,5-dione ions can easily be explained by the fragmentation phenomena and adduct formation observed for imides.[37]

The isolated yields and the calculated purities of the synthesised piperazine-2,5-diones (**4a**-**4m**) and dipotassium pyrazine-2,5-bis(olates) (**6a**-**6m**) are depicted in Table S1 given in the supplementary data. The synthesis of the conjugated piperazine-2,5-diones (**4a**-**4m**) was successful for both symmetrical and unsymmetrical compounds, with yields ranging from 52–95% and purities ranging from 81–99%. The NMR results of **4a**-**4e** suggest that these, and presumably the rest of the synthesised piperazine-2,5-diones, were obtained as one of the four possible diastereomers, i.e. either the *Z,Z*-, *E,Z*-, *Z,E*- or *E,E*-isomer. According to literature, the *Z,Z*-isomer is the most likely to form during the elimination of acetic acid from an intermediary during the reaction, possibly due to intramolecular hydrogen bonding.[27] Furthermore, the formation of the *Z,Z*-isomer is also considered more thermodynamically favourable.[38] It is therefore assumed that the *Z,Z*-isomer is the most prevalent isomer present and further discussions are beyond the scope of this text.



1 **2** **3a - 3m** **4a - 4m** **6a - 6m**

Compound	**R₁**	**R₂**
3a - 6a	phenyl	phenyl
3b - 6b	2-pyridinyl	2-pyridinyl
3c - 6c	2-thienyl	2-thienyl
3d - 6d	2-furyl	2-furyl
3e - 6e	4-formylphenyl	4-formylphenyl
3f - 6f	4-carboxyphenyl (k salt)	4-carboxyphenyl (k salt)
3g - 6g	4-nitrophenyl	4-nitrophenyl
3h - 6h	4-cyanophenyl	4-cyanophenyl
3i - 6i	4-(dimethylamino)phenyl	4-(dimethylamino)phenyl
3j - 6j	2-thienyl	4-carboxyphenyl (k salt)
3k - 6k	2-thienyl	4-nitrophenyl
3l - 6l	2-thienyl	4-cyanophenyl
3m - 6m	2-thienyl	4-(dimethylamino)phenyl

Scheme 2. Synthesis route of dipotassium pyrazine-2,5-bis(olates), **6a**-**6m**.

Although products **4a**-**4m** were relatively pure, 70–90% based on ^{1}H NMR, this degree of purity is considered insufficient for use as organic semiconductors. Consequently, a purification method was developed to increase the purity to >95%. Although the method proved successful for most compounds, it was inadequate in the cases of **4i** and **4m**. In the case of **4i**, this is likely due to the solubility of the parent aldehyde matching that of the product in the pH range utilised during the isolation. A similar argument may explain the presence of the unidentified benzylamine derivative present in **4m**.

The low solubility of **4a**–**4m**, prevented their NMR spectra from being recorded. However, the synthesis of the compounds is confirmed by the results of their HR-MS spectra, as well as the HR-MS and NMR spectra recorded for their dipotassium pyrazine-2,5-bis(olate) derivatives (**6a**-**6m**), which corroborated that the intermediate compounds **4a**-**4m** were successfully synthesized.

It was suggested that the existence of the imide tautomers of piperazine-2,5-diones could explain the susceptibility of the piperazine-2,5-dione core to condensation reactions.[27] Bowman *et al.*,[41] and Liu *et al.*,[24] proved this hypothesis since they proved that the necessary molecular conformation for the synthesis of the *p*-azaquinodimethane derivatives were present.[24, 26, 39] Numerous other publications regarding the synthesis of *p*-azaquinodimethanes also substantiate the claim that the piperazine-2,5-diones prefer to assume an imidate structure under the alkaline reaction conditions utilised during these syntheses, although the anions in solution can be described by two mesomeric forms.[24-26, 29]

The preparation and isolation of the potassium imidate derivatives of the highly conjugated piperazine-2,5-diones in this study were relatively uncomplicated, and the formation of the dipotassium pyrazine-2,5-bis(olate) occurred irrespective of the conjugated groups attached to the core. Considering the work reported by Liu *et al.*, 4 eq. of a haloalkane, and 10 eq. of a potassium (i.e. 5 eq. of K_2CO_3) salt and starting piperazine-2,5-dione in DMF at a concentration of 0.11 M, were required to synthesise **7** in yields between 52-61%, upon heating the reaction mixture to 100 °C for 2 hours.[24] In comparison, during the preparation of **6** by the method discussed in this work, no haloalkanes were utilised, only 2-4 eq. of a potassium (i.e. 2-4 eq. of KO^{t}Bu) salt and the starting piperazine-2,5-dione in methanol, or ethanol, at a concentration of 4.92 M, were utilised. The preparation of the dipotassium pyrazine-2,5-bis(olate) core also delivered a greater yield of the desired quinoidal compound, as quantitative yields were obtained during the mechanochemical synthesis of **6**, compared to the 52-61% yields obtained for **7** as indicated in the literature.[24]

Preparation of the pyrazine-2,5-bis(olates), **6a**-**6m**, was possible without the use of a solvent, however, to ensure complete salt formation, methanol was utilised to facilitate adequate mixing. The base of choice during this study was KO^{t}Bu, as the reaction formed ^{t}BuOH was easier to remove than water that would have formed had a hydroxy-base been utilised.

An interesting phenomenon was observed in the mass spectra (see supporting information) of the pyrazine-2,5-bis(olates), **6a**-**6m**; the masses of the observed ions correlate to those of their corresponding piperazine-2,5-diones, **4a**-**4m**. No mass fragments corresponding to the mono- or dipotassium adducts were observed; however, the free pyrazine-2,5-bis(olate) core was protonated when utilising both negative and positive ionisation techniques. Consequently, the resulting negative and positive ion mass spectra showed the molecular ion as $[M+2H-H]^-$ or $[M+2H+H]^+$, respectively. This likely occurs due to hydrogen adduct formation in the ionisation source; however, this requires further investigation, possibly through MALDI-TOF MS.[40]

Two ions seem to be characteristic of the pyrazine-2,5-bis(olates), **6a**-**6m**, namely, m/z = 73 and m/z = 103; these m/z values correspond to molecular formulas of C_3H_7NO and $C_4H_{11}N_2O$, respectively. Fragments with these masses are not commonly present in the mass spectra of the conjugated piperazine-2,5-diones, **4a**-**4m**, nor are they present in the mass spectra of non-conjugated piperazine-2,5-diones described in the literature.[41] However, these fragments are present in several positive ion spectra of the dipotassium pyrazine-2,5-bis(olates). The MS and NMR results also suggested that the piperazine-2,5-dione core did not undergo ring-opening during the preparation of the dipotassium pyrazine-2,5-bis(olates), which may have occurred had the amidic bond been hydrolysed.

The formation of the quinoidal pyrazine-2,5-bis(olates) was also marked by distinct visual changes observed during salt formation. A darkening in the colour, or a prominent colour shift, was consistently observed in all compounds when they were converted from the piperazine-2,5-dione (**4a**-**4m**) to the dipotassium pyrazine-2,5-bis(olate) (**6a**-**6m**), **Table 1**. This change is indicative of an alteration in the electronic structure, likely arising from a reduction in the band gap during the formation of the quinoidal framework, echoing previous studies on *p*-azaquinodimethane derivatives.[24] The most prominent colour changes were observed for **6e**, **6g**, **6h**, and **6k**, all of which contain electronegative substituents, i.e. carboxaldehyde (**6e**), nitro (**6g** and **6k**), or cyano (**6h**).

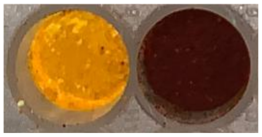
Table 1. Colour change when converting the piperazine-2,5-diones (**4a-4m**), to their corresponding dipotassium pyrazine-2,5-bis(olates) (**6a-6m**)


4a 6a


4b 6b


4c 6c


4d 6d


4e 6e


4f 6f


4g 6g

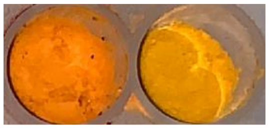

4h 6h


4i 6i


4j 6j


4k 6k


4l 6l


4m 6m

These visual changes were corroborated by UV-Vis-NIR diffuse reflectance spectroscopy, which provided evidence of a red shift in the maximum absorption wavelength as conversion from the neutral to the salt form took place. The red shift suggested a narrowing band gap associated with the stabilization of the compounds in a quinoidal core structure as illustrated in Figure 4. The bathochromic behaviour reinforced the argument that the structural transformation to the quinoidal imidate framework alters both the molecular charge transfer and optical properties, consistent with previous reports. The melting points, or carbonisation points, of the dipotassium pyrazine-2,5-bis(olate) derivatives were generally also higher than those observed for the piperazine-2,5-dione derivatives. Although it was possible to obtain crystallographic evidence for the formation of the dipotassium pyrazine-2,5-bis(olate) **6a** (see Table S2 and Figure S1 in the Supporting Information) the moisture and temperature instability of the crystals made it impossible to adequately define the crystal parameters. Consequently, this data was not deemed worthy of publication and only serves to support the claims of this work.

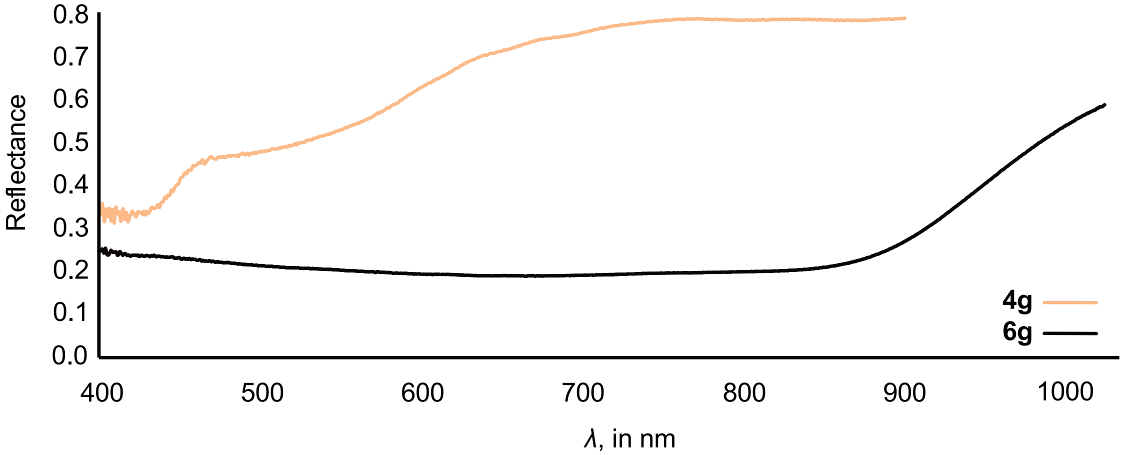


Figure 4. Overlayed UV-Vis-NIR diffuse reflectance spectra of **4g** and **6g**.

After preparation of the dipotassium pyrazine-2,5-bis(olates), their solubility in polar solvents, specifically DMSO and DMF and sometimes in ethanol, methanol, and water, was also improved significantly, attributed to an increase in the polarity of the molecules. Finally, the shifts observed in the ATR (Figure 5a) and NMR spectra (Figure 5b) implied that the bonds between the atoms, as well as the electronic environment of the atoms, differ between the piperazine-2,5-dione core and the dipotassium pyrazine-2,5-bis(olate) core.

The distinctive amide fingerprint of precursor **4a** is easily recognised in its ATR-FTIR spectrum with a medium amide II band (N–H bend + C–N stretch) at 1494 cm^{-1}, a sharp amide III feature at 1353 cm^{-1}, as well as a strong amide I (C═O stretch) at 1678 cm^{-1}. Furthermore, two wide signals with centres at 3351 and 3166 cm^{-1} are indicative of the secondary-amide N–H stretch. Following conversion to the dipotassium salt **6a**, none of these absorptions are preserved. Rather, at 1649 cm^{-1}, a new, strong band appears that is unmistakably the quinoidal ketimine/imidate moiety's C═N stretching vibration. A band at 1391 cm^{-1} is indicative of the imidate C–O(K$^+$) stretch and a shoulder at 1594 cm^{-1} is attributed to the conjugated C═C stretch of the azaquinonoid backbone. The conversion to the quinoidal imidate is well-matched with the downshift of the carbonyl-derived vibration by around 30 cm^{-1} (from 1678 cm^{-1} to 1649 cm^{-1}), which indicates the loss of the amide carbonyl resonance and the creation of an electron-rich C═N bond. When combined, the simultaneous development of the C═N and C–O(K$^+$) absorptions and the elimination of the amide I–III and N–H bands, offer strong proof that the desired quinoidal framework was successfully synthesised in **6a**.

Compounds **4a**-**4m** are relatively insoluble in common organic solvents and water, with **4c** and **4d** being exceptions, as they are slightly soluble in chloroform and DMSO. Upon conversion to the dipotassium pyrazine-2,5-bis(olates) **6a**-**6m**, the solubility of most of the compounds dramatically increased in DMSO and DMF. However, even after conversion, the carboxylic acid-containing compounds, **6f** and **6j**, were practically insoluble in DMSO and DMF but completely soluble in deionised water. The solubility of **6f** and **6j** in DMSO and DMF increased upon the addition of water, where a ratio of 1:3, water:DMSO or water:DMF, resulted in complete dissolution. The improved solubility of **6a**-**6m** over that of **4a**-**4m**, either originates due to ionisation phenomena, or due to solvent coordination breaking the π-π stacking that exists in the piperazine-2,5-diones.

NMR of the piperazine-2,5-diones **4a**-**4m**, as well as the pyrazine-2,5-bis(olates) **6a**-**6m** was complicated by numerous factors. As noted, many of the piperazine-2,5-diones were insoluble in common solvents and it was found that trifluoroacetic acid (deuterated) was the only solvent that could dissolve enough for NMR analysis. In many cases, the resulting spectra were significantly convoluted, and the definitive peak assignment was complicated, as is exemplified by **4a** in Figure 5b.

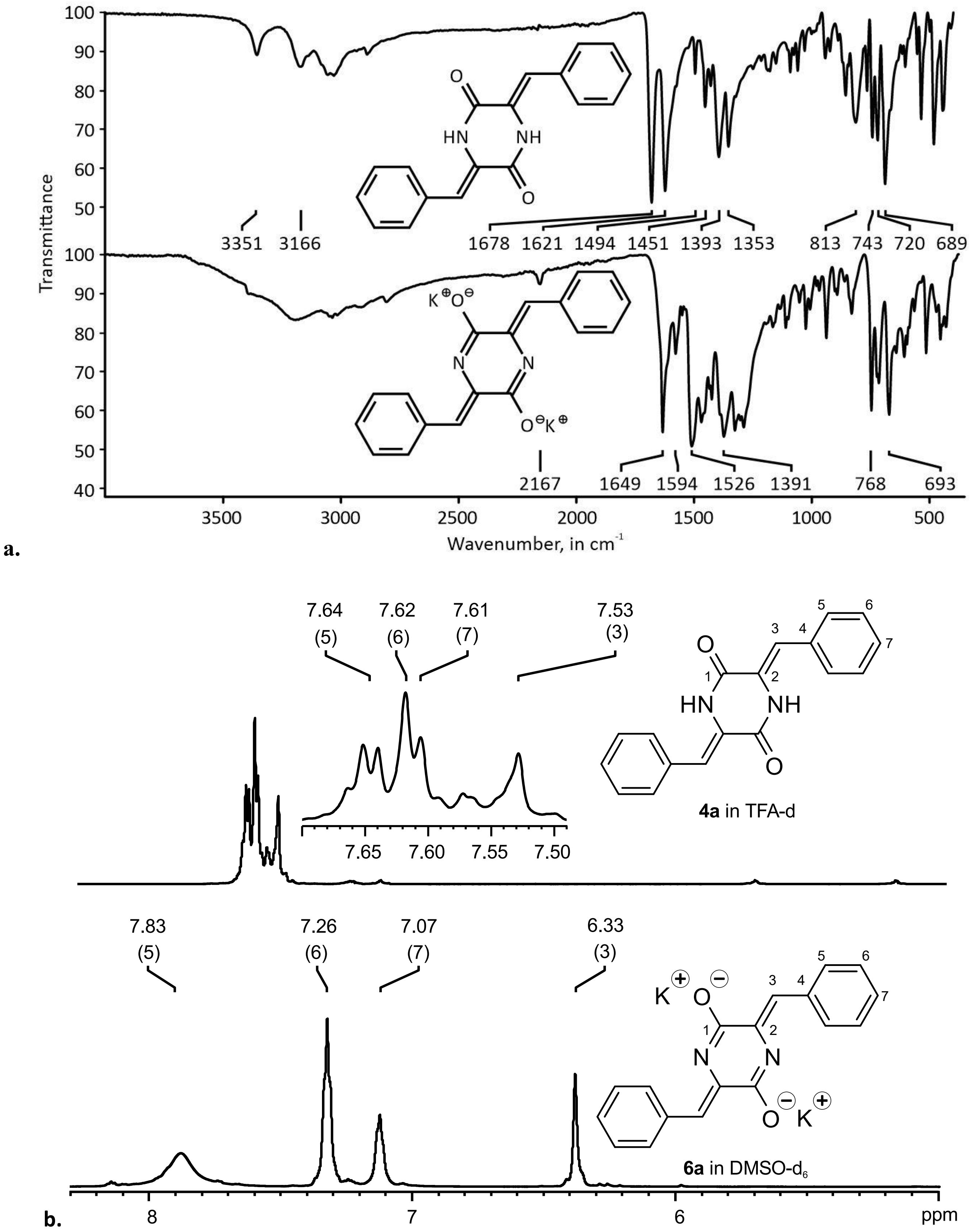
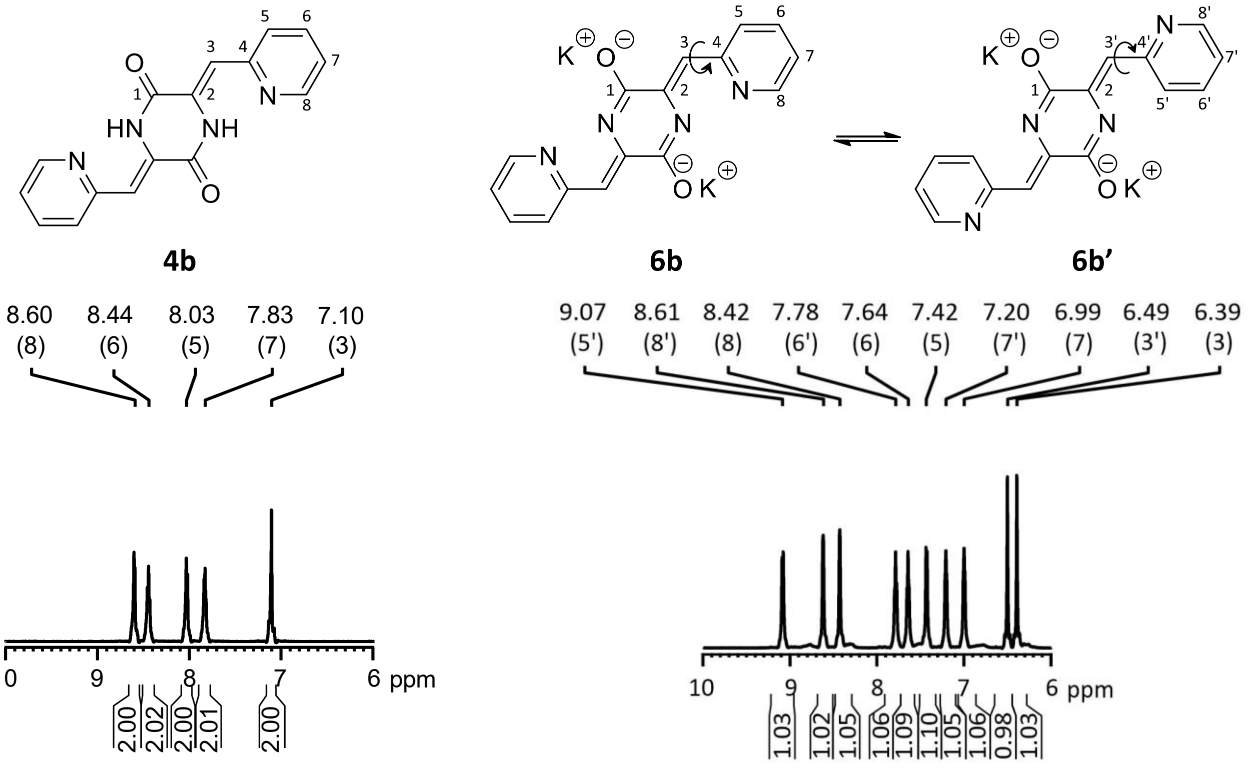


Figure 5. **a**. Overlayed FTIR of **4a** and **6a**, clearly illustrate the disappearance of the amide carbonyl stretch to the and formation of imidate ketimine stretch. b. Overlayed ^{1}H NMR of **4a** in TFA-d and **6a** in DMSO-d_6.

Regarding the pyrazine-2,5-bis(olates) **6a**-**6m**, solubility in DMSO-d_6 or D_2O was markedly improved over their precursors. The same phenomenon occurred in the case of **4c**, where the shift of carbon 4 is almost hidden in the baseline. The ^{13}C NMR spectrum of **6c** also presented with missing shifts; yet, after examination of the HSQC data, the shifts of carbons coupled to hydrogens became more visible. The ^{13}C NMR spectrum of **6c** also presented with broadening of signals, with the shifts of carbon 5, 6, and 7 overlapping, which is attributed to interconversion between two rotamers.

Beyond general structural confirmation, a closer examination of specific NMR spectra showed unusual duplication patterns in certain derivatives, prompting a more detailed analysis of conformational effects. The NMR spectra of some salts bearing heteroaromatic groups, (**6b**–**6d** and **6l**) showed doubling of particular signals, which were shifted slightly from one another, implying the presence of possible rotamers. In the case of **6b**, this phenomenon is most evident since well-resolved double peaks of equal intensity were observed, suggesting a 1:1 rotamer distribution (Figure 6). **6l** showed minor secondary signals of approximately one-sixth the intensity of the main component. Compounds **6c** and **6d** did not show resolved peaks and were mostly reflected as signal broadening. This behaviour can be explained by considering the existence of rotamers resulting from limited rotation around the central bond of the extended conjugated system (C3-C4, Figure 6).

The extent of signal splitting appears to correlate with both the steric and electronic properties of the heteroaryl substituents. In particular, the pyridin-2-yl group in **6b** introduces greater steric hindrance than the five-membered furan or thiophene rings (**6c** and **6d**). This increases the likelihood of distinct spatial orientations relative to the pyrazine core, especially for the aromatic protons of the pyridine ring, which lies in closer proximity to the quinoidal system. The electron-rich nitrogen and its lone pair electrons can interact with adjacent π-systems, further influencing shielding effects. The resulting conformational asymmetry places the protons in two chemically distinct environments across the rotamers, accounting for the observed peak splitting in the ^{1}H NMR spectrum. This interpretation is further supported by the molecular planarity and extensive conjugation of the quinoidal scaffold, which promotes discrete low energy rotamers with torsional angles of 0° or 180°, optimising orbital overlap.[42] Moreover, the use of DMSO-d_6 may stabilise these conformers or reduce their interconversion rate, allowing both to be resolved on the NMR timescale. In the same vein as this argument, the heteroatoms present in these substituents, specifically nitrogen, sulphur and oxygen, may coordinate to the potassium ions in solution, thereby also stabilising the conformers.



4b in TFA-d

6b in DMSO-d_6

Figure 6. ^{1}H NMR of **4b** in TFA-d and **6b** in DMSO-d_6.

Another justification for the assumption that solvent-based stabilisation of rotamers results in this phenomenon lies in the solvent-induced convergence of the aromatic hydrogen shifts in the ^{1}H NMR of **6g**, Figure 7. An NMR spectrum of the **6g**, before the removal of excess ^{t}BuOH, demonstrated the influence of the solvent system on the observed NMR shifts. Shift averaging occurs for the aromatic protons in the ^{1}H NMR of **6g** with excess ^{t}BuOH, Figure 7a, whereas two explicit aromatic shifts are visible, although ill-defined, in the ^{1}H NMR of **6g** without excess ^{t}BuOH, Figure 7b.

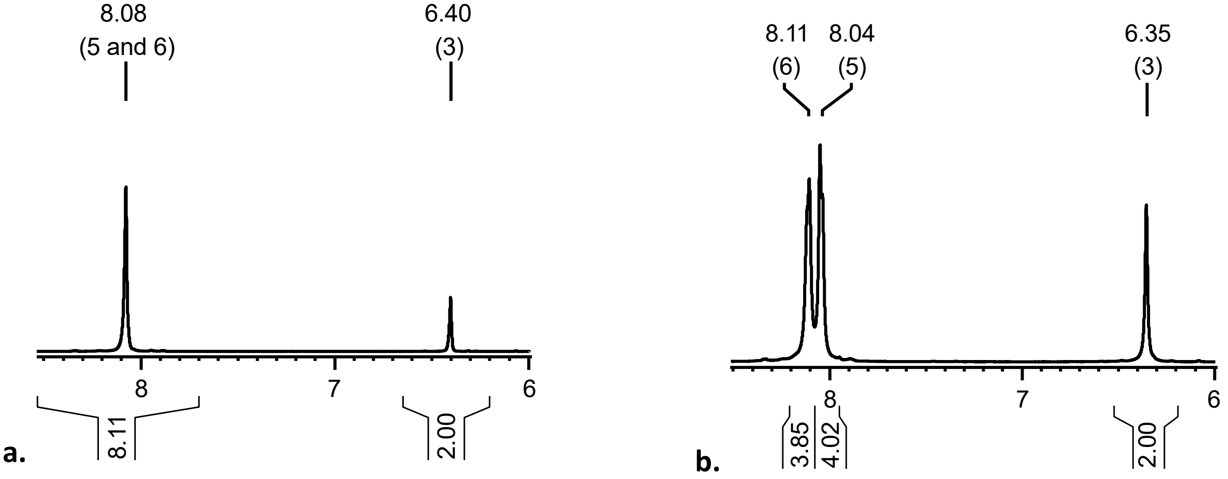


Figure 7. **a.** 1H NMR of **6g** with excess tBuOH. **b.** 1H NMR of **6g** without excess ^{t}BuOH. Both spectra were recorded in DMSO-d_6.

Conclusions

This study presents the first systematic synthesis, isolation, and characterisation of a series of dipotassium pyrazine-2,5-bis(olates), derived from conjugated piperazine-2,5-diones. The work demonstrates that these salts can be prepared under relatively mild conditions using a mechanochemical protocol, thereby avoiding some the limitations associated with previously reported p-azaquinodimethane synthesis routes. Spectroscopic and analytical characterisation, including FTIR, NMR, MS, and UV-Vis-NIR diffuse reflectance spectroscopy, confirmed the formation of the quinoidal core and supports the observed changes in electronic structure, solubility, and colour. Additionally, not only did the synthetic route developed replaced toxic solvents, such as DMF, it also increased the yields, at reduced times and temperature making this a more sustainable preparation method for quinoidal semiconductors.

The combination of enhanced solubility in polar solvents, improved synthetic accessibility, and structural features consistent with conjugated quinoidal frameworks positions these compounds as valuable scaffolds for future development in organic electronics, particularly in the context of mixed ionic-electronic conducting materials. This work contributes a new pathway to the design of quinoidal materials and forms the foundation for their broader application across materials science and electronic device engineering.

Experimental Section

Chemicals and instrumentation. All chemicals were purchased from Merck Life Science (Pty) Ltd unless stated otherwise. All chemicals utilised for analysis were of analytical grade. A Metrohm 914 pH/conductometer or a Merck Mquant® universal pH indicator strips, pH 0–14, were utilised for pH measurements. A Büchi B-545 melting point apparatus, with an analytical range of 0–400 °C, was utilised to determine the uncorrected melting points (M.P.) of all solid samples.

Atmospheric pressure chemical ionisation mass spectrometry (APCI-MS) analyses were conducted utilising a Bruker MicroTOF-QII mass spectrometer. The scan range was from 50–500 *m/z* and the ion polarity was set to either positive or negative, as indicated on respective spectra. The potential of the capillary was set at 3.0 kV for negative ion spectra and 4.5 kV for positive ion spectra, whereas the endplate offset was set at -0.50 kV in both cases. The collision cell RF was set at 100 Vpp, the nebuliser was set at 1.6 bar, the dry heater was set at 200 °C and the dry gas was set to a flow rate of 8 $L \cdot min^{-1}$. Electrospray ionisation (ESI) mass spectrometry analyses were conducted with a micrOTOF-Q II™ ESI-Qq-TOF mass spectrometer. The scan range was from 50–1 600 *m/z* and the ion polarity were either set to positive or negative, as indicated on the respective spectra. The capillary potential was set at 2.60 kV for compounds **6f** and **6j**, whereas the capillary potential was set at 4.50 kV for compound **3i –** compound numbers follow below. The endplate offset was set at -0.50 kV. The collision cell RF was set to 110 Vpp, the nebuliser pressure was set at 0.80 bar, the dry heater was set at 200 °C and the flow rate of the dry gas was set at 4 $L \cdot min^{-1}$. A Bruker Alpha-P ATR-FTIR was used for IR analyses. Liquid samples were placed on the sample window, while solid samples were compressed onto the sample window.

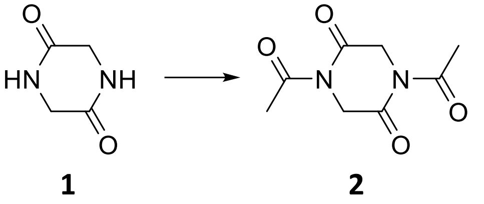
NMR experiments were performed utilising a Bruker Avance NEO 600 MHz spectrometer. Spectra were recorded with a 2-channel broadband, direct observation iProbe at 600 MHz for ^{1}H NMR and at 150 MHz for ^{13}C NMR. The chemical shift values are reported in parts per million, ppm, and the chemical shift values of the residual non-deuterated solvents were utilised as the chemical shit references; trifluoroacetic acid-*d* (^{1}H: δ 11.50 ppm, singlet; ^{13}C: δ 164.20 ppm, quartet), dimethyl sulfoxide-d_6 (^{1}H: δ 2.50 ppm, singlet; ^{13}C: δ 39.51

ppm, septet) and D_2O (^{1}H: δ 4.81 ppm, singlet; MeOH acted as the reference solvent ^{13}C: δ 49.15 ppm, septet). The measurement temperature was maintained at 25 °C.

The UV-Vis-NIR diffuse reflectance spectra were recorded on a Specord S 600 spectrophotometer, Analytik Jena GmbH+Co (Thuringia, Germany), with an integrating sphere. Dark current correction was applied to all analyses, the accumulation was set to 5, and the integration time was set to 5000 ms. All samples were ground to a fine powder and then transferred to the sample cavity. There it was lightly compressed and levelled with the upper edge of the sample cavity before analyses. The analytical range of the instrument ranged 400–1100 nm; however, as none of the piperazine-2,5-diones presented with NIR absorbance, an upper cutoff was set for these compounds at 900 nm.

Synthesis methods.

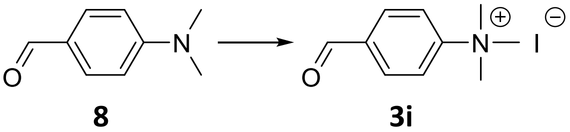
1,4-Diacetylpiperazine-2,5-dione (2)



Scheme 2. Synthesis of 1,4-diacetylpiperazine-2,5-dione (**2**).

The method utilised for the synthesis of 1,4-diacetylpiperazine-2,5-dione, **2** in Scheme 2, was adapted from literature.[43] Briefly, 49.5 g (0.43 mol, 1 eq.) of piperazine-2,5-dione (**1**) was suspended in 400 mL (4.23 mol, 9.83 eq.) of acetic anhydride. This mixture was placed in an oil bath, preheated to 150 °C, and refluxed under argon for 5 h, with vigorous stirring. After completion of the reaction, the reaction mixture was concentrated under vacuum at 60 °C. To remove any remaining acetic acid, the resulting solid was dispersed in 100 mL of ethanol and the mixture was once again concentrated under vacuum at 60 °C. The product was utilised in subsequent reactions without further purification.

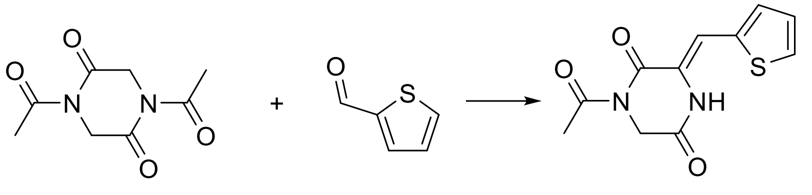
4-Formyl-*N*,*N*,*N*-trimethylanilinium iodide (3i)



Scheme 3. Synthesis of 4-formyl-*N,N,N*-trimethylanilinium iodide (**3i**).

The method utilised for the synthesis of 4-formyl-*N*,*N*,*N*-trimethylanilinium iodide, **3i** in Scheme 3, was reported previously.[44] Briefly, 50 g (0.33 mol, 1 eq.) of 4-(dimethylamino)benzaldehyde (**8**) was stirred in approximately 450 mL of acetone (18 eq.) Subsequently, 105 mL of iodomethane (1.66 mol, 5 eq.) was added. The reaction vessel was purged with argon, sealed and heated to 70 °C for 8 h. Upon completion of the reaction, the precipitate was filtered off and washed with excess acetone and subsequently recrystallised out of methanol.

(3*Z*)-1-acetyl-3-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (9)



2 **3c** **9**

Scheme 4. Synthesis of (3*Z*)-1-acetyl-3-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (**9**).

The method utilised for the synthesis of (3*Z*)-1-acetyl-3-[(thiophen-2-yl)methylidene]piperazine-2,5-dione, **9** in Scheme 5, was adapted from the method utilised by Katritzky *et al.*[45] Briefly, 43.1 g (0.22 mol, 1 eq.) of 1,4-diacetylpiperazine-2,5-dione (**2**) was stirred vigorously with 24.4 g (0.22 mol, 1 eq.) thiophene-2-carbaldehyde (**3c**). Subsequently, 22 g (0.22 mol, 1 eq.) of TEA was added, and the reaction mixture was stirred under argon, at room temperature for 8 h.

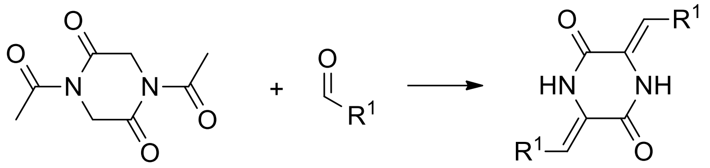
After completion of the reaction, an excess of cold, deionised water was added to the reaction mixture. The resulting precipitate was filtered off and washed with excess water, then with a small volume of ethanol and dried at 70 °C for 5 h.

Symmetrical conjugated piperazine-2,5-diones (4a-4i)

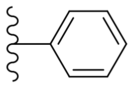
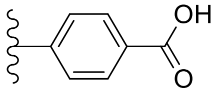
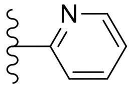
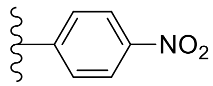
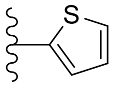
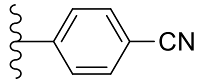
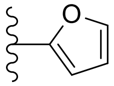
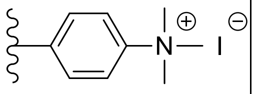
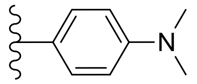
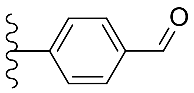
The method utilised for the synthesis of the symmetrical piperazine-2,5-dione derivatives, Scheme 4, was adapted from the method utilised by Liu *et al.*[24] Shortly, 1 eq. of 1,4-diacetylpiperazine-2,5-dione (**2**) was stirred with 2.2–2.5 eq. of an aromatic aldehyde (**3a**-**3i**) at room temperature. Subsequently, 5.4 mL of DMF, per 1 mmol of 1,4-diacetylpiperazine-2,5-dione (**2**) was added to the reaction mixture. The reaction mixture was heated to 120–150 °C in an oil bath, under an argon atmosphere.

After reaching the desired temperature, 4–6 eq. of TEA was added in small increments. The general procedure required 2 eq. of TEA per aromatic aldehyde, however, when an aromatic aldehyde containing a carboxylic acid was utilised 3 eq. of TEA was added per eq. of carboxylic acid containing aromatic aldehyde. After the addition of the TEA, the reaction mixture was stirred within the aforementioned temperature range for 16 h.

After completion of the reaction, the reaction mixture was allowed to cool to room temperature followed by the addition of an excess of deionised water. The resulting precipitate that formed was filtered off, washed once with a small volume of DMF, three times with ethanol, and finally with acetone. The filter cake was pulverized and dried at 70 °C for 2 h, yielding the crude products.



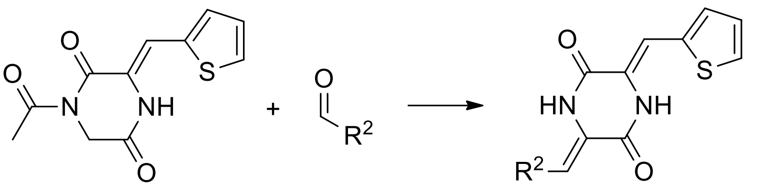
2 **3a - 3i** **4a - 4i**

R^1	Mass of **2** (g)	Mass of **3** (g)	R^1	Mass of **2** (g)	Mass of **3** (g)
 **3a** and **4a**	8.0	10.8	 OH O **3f** and **4f**	2.4	4.0
 N **3b** and **4b**	4.0	5.4	 NO$_2$ **3g** and **4g**	2.5	4.6
 S **3c** and **4c**	4.0	5.7	 CN **3h** and **4h**	6.9	10.3
 O **3d** and **4d**	4.0	4.9	 N I **3i** and  N **4i**	5.4	17.4
 O **3e** and **4e**	7.4	11.1			

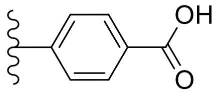
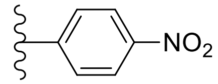
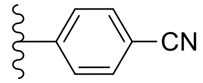
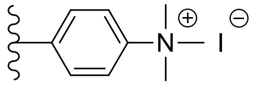
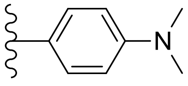
Scheme 5. Synthesis of symmetrical piperazine-2,5-diones (**4a-4i**).

In the case of **4c** and **4d** washing with DMF was avoided, as these compounds are slightly soluble in DMF. In the case of **4i** the solvent was evaporated after completion of the reaction, then the reaction concentrate was diluted with acetone and filtered. The filter cake was washed with deionised water three times and finally with acetone, before drying.

Unsymmetrical conjugated piperazine-2,5-dione derivatives (4j-4m)



2 **3f - 3i** **4j - 4m**

R^2	Mass of **9** (g)	Mass of **3** (g)
 **3f** and **4j**	10.1	6.1
 **3g** and **4k**	7.0	4.2
 **3h** and **4l**	10.0	5.3
 **and**  **3m** **4m**	7.0	8.1

Scheme 6. Synthesis of unsymmetrical piperazine-2,5-diones (**4j-4m**).

The method utilised for the synthesis of the unsymmetrical piperazine-2,5-dione derivatives, **4j-4m** in Scheme 6, was adapted from literature.[45] Briefly, 1 eq. of (3*Z*)-1-acetyl-3-[(thiophen-2-yl)methylidene]piperazine-2,5-dione (**9**) was combined with DMF in a ratio of 5.4 mL DMF per 1 mmol of **9**. The resulting mixture was heated to 120–150 °C, under argon, with constant stirring. Once all the solid material had dissolved, the aromatic aldehyde (**3f**-**3i**) was added to the reaction mixture in a 1.1 eq., followed by 2 eq. of TEA where **3f**, **3g** and **3h** underwent condensation with **9**, or 3 eq. of TEA where **3i** underwent condensation with **9**.

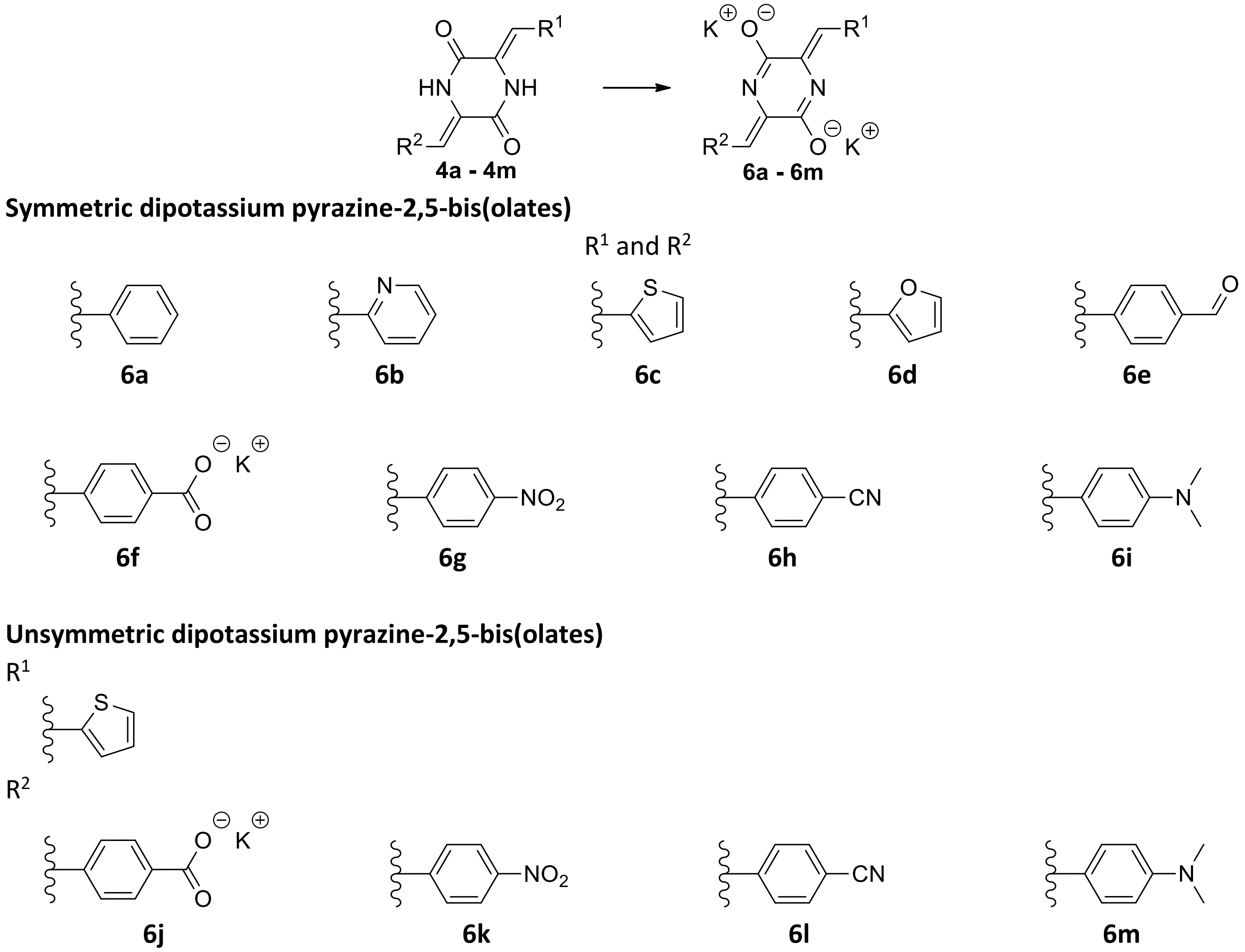
After the addition of TEA, the reaction mixture was stirred between 120–150 °C for 16 h. Subsequently, the reaction mixture was allowed to cool to room temperature before adding an excess of cold, deionised water. A precipitate formed, which was filtered out of the reaction mixture. The filter cake was washed once with DMF, three times with ethanol and once with acetone. The filter cake was then dried at 70 °C for 2 h to deliver the products.

In the case of **4m**, the reaction mixture was concentrated to dryness using rotary evaporation. Subsequently, the concentrate was redispersed in acetone and filtered, and the resulting filter cake was washed twice with acetone. Based on ^{1}H-NMR, the purities of **4a**-**4m** were between 70–90%. However, impurities may act as product traps during intermolecular charge transfer in organic semiconductors, therefore a purification method was devoted to increase the average purity to ≥ 95%.

Purification of the conjugated piperazine-2,5-dione derivatives (4a-4m)

The dried piperazine-2,5-diones (**4a**-**4m**) were weighed and combined with 2.3–4.3 eq. of potassium hydroxide. The general method required 2.3 eq. of KOH; however, in cases where carboxylic acids were present in the molecule, one eq. of KOH was added per carboxylic acid group. Subsequently, 60–360 mL of ethanol was added, and the mixture was stirred until the KOH was completely dissolved. Subsequently, 20–440 mL of DMF was added, based on the volume required to result in the complete dissolution of the product. In the case of **4f** and **4j**, 125 mL of deionised water was added for complete dissolution of the product. Following complete dissolution, the mixture was filtered through a pore-size 3-sintered glass funnel to remove any solid impurities.

Dipotassium pyrazine-2,5-bis(olates) (6a-6m)



Scheme 7. Solvent-assisted mechanochemical preparation of dipotassium pyrazine-2,5-bis(olates), **6a-6m**.

To precipitate the pure products, the filtrate was stirred vigorously and titrated to a pH of 7 using a 1:1 mixture of concentrated HCl and ethanol. The resulting precipitate was separated by filtration through Celite® 545. The product was protected from direct contact with Celite® by covering the Celite® with two grade 1

Whatman® filter papers. Following filtration, the product was washed twice with deionised water and three times with ethanol and then dried at 80 °C for 2 h.

In the case of compounds containing carboxylic acids, titration of the acidic methanol was continued to a pH ≤ 1 and the precipitate was washed with deionised water until the filtrate had a pH of 7. For compounds containing amines, the titration of acidic methanol was stopped at pH 7. Hereafter, excess deionised water was added to the mixture to facilitate the precipitation of the products.

Scheme 7 depicts the synthesis method developed for the dipotassium pyrazine-2,5-bis(olates). All conversions were completed utilising 1 g of the respective piperazine-2,5-diones (**4a**-**4m**). Shortly, 1 eq. of the selected piperazine-2,5-dione (**4a**-**4m**) was crushed with 2-4 eq. of KO^{t}Bu, potassium hydroxide or potassium carbonate until a visible and homogeneous colour change was observed throughout the mixture. Subsequently, 8 eq. of methanol was added, and the resulting mixture was stirred for 1 min. Subsequently, the mixture was dried under a vacuum at 80 °C. Refer to the supplementary material for the characterization of the products.

Acknowledgements

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Supplementary Material

Supporting Information File: Compound characterization data (FTIR, HRMS, ^{1}H NMR, ^{13}C NMR, DEPT, HSQC and in the case of **6a** single crystal XRD) of synthesized compounds.

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