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An alternative method to access diverse *N*,*N*′-diquaternised-3,3′-biquinoxalinium "biquinoxen" dications†

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An alternative synthetic route for the design of *N*,*N*′-diquaternised-3,3′-biquinoxalinium "biquinoxen" dications is reported, involving oxidative radical coupling of dithionite reduced quinoxaline quaternary salts. Although the reaction is not regioselective, leading to relatively modest yields (up to 32%), the advantages of this new synthetic protocol lie in a simple potentially gram scale synthesis using inexpensive easily accessible reagents with no metal catalysts and no purification steps. Thus whereas the method reported previously to access the *N*,*N*′-dimethyl-3,3′-biquinoxalinium, "methylbiquinoxen" precursor gave higher yield than the new method reported here, this new method avoids the limitation of using scarce oxonium reagents. Overall, the new protocol is a robust synthetic strategy which offers new design possibilities.

Introduction

Combining the redox activity of viologens[1] in concert with the chelating function of a simple organic ligand such as 2,2′-bipyridine is an important challenge since it would provide a unique opportunity to create robust metal/ligand complexes with exotic and tuneable electronic structures. This would produce strongly correlated phenomena between the ligand and any metalloid centre with potential applications such as in spin labelling, catalysis or molecular magnetism.

In this context, since the pioneering work of Kaim on 3,3′-bipyrazinium and 4,4′-bipyrimidinium based chelates and their studies as spin labels,[2–4] we reported a new multi-functional chelating organic ligand, the *N*,*N*′-dimethyl-3,3′-biquinoxalinium "methylbiquinoxen" dication, (**Mbqn**$^{2+}$), the first member of a new family of 3,3′-biquinoxalinium diquaternary salts coined "biquinoxens" (Fig. 1). Surprisingly, such a simple and stable pro-ligand revealed a promising versatility.

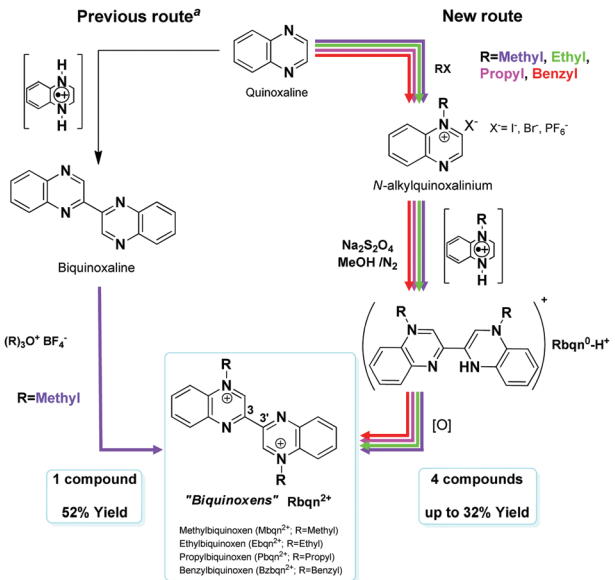

Fig. 1 Previous route (left path) as reported and discussed in ref. 5[a] for the synthesis of the methylbiquinoxen **Mbqn**$^{2+}$ only. Alternative and more versatile (right path) synthetic route for the design of various *N*,*N*′-disubstituted-3,3′-biquinoxalinium "biquinoxens" **Rbqn**$^{2+}$ with R = methyl, ethyl, propyl and benzyl.

Indeed the **Mbqn**$^{2+}$ platform proved not only to combine a rich redox and Lewis acid/base chemistry combined with the chelating functionality, but also shows tuneable luminescence as well as providing the possibility of covalent functionalisation similar to the "click" chemistry approach.[5,6]

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† Electronic supplementary information (ESI) available: Complete synthesis, tables of crystal and X-ray crystallographic files in CIF format, XRPD patterns, UV-Vis and IR spectra of [**Rbqn**$^{2+}$](BF$_4$)$_2$ (R = Me, Et, P, Bz), additional EPR spectra, elemental analysis and DFT calculation of the intermediate species. CCDC 1511787–1511789. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7nj00531h

Furthermore, besides being simple to synthesise in a pure form, in good yield and gram quantities in as little as two steps, the multiple properties are anchored on the same 1,4-diazine core structure of the **Mbqn**$^{2+}$ which offers exciting prospects for the design of organic or hybrid organic–inorganic based molecular compounds with interconnected and synchronous properties.

In terms of the synthesis, the diquaternisation of biquinoxaline[7] using Meerwein alkylation was found to be the easiest way to obtain **Mbqn**$^{2+}$ (Fig. 1). However, extension of this method to target other diquaternised biquinoxens is clearly limited due to the poor nucleophilicity of biquinoxaline, substantiated by the fact that very few biquinoxaline-based coordination complexes have been reported and mostly use diamagnetic metal ions.[8,9] Thus, although using oxonium derivatives as a last resort proved to be a remarkably successful pathway to target the desired **Mbqn**$^{2+}$, such strong alkylating agents are scarce and mostly not commercially available. This significantly hinders current access to the synthesis of further members of this family using the left hand route in Fig. 1 and therefore we explored an alternative route.

In the context of the potential of biquinoxens derivatives and the challenges to be addressed, we report here a novel route to design *N*,*N*′-diquaternised biquinoxens, which instead of using biquinoxaline involves the oxidative radical coupling of chemically reduced quinoxaline quaternary salts (Fig. 1).

Following this new method, joining the broad family of oxidative radical cross-coupling reactions,[10] we have been able to reproduce the Mbqn precursor and to get three new homologues, namely ethylbiquinoxen (**Ebqn**$^{2+}$), propylbiquinoxen (**Pbqn**$^{2+}$) and benzylbiquinoxen (**Bzbqn**$^{2+}$). Since the chemistry of quinoxaline quaternary salts is well-known but demanding in terms of synthesis,[11] the purpose of this paper is to introduce this alternative method rather than presenting the whole library of biquinoxens which can be synthesised in this way.

Results and discussion

Synthetic procedures

Compounds **Rbqn**$^{2+}$ (R = M (methyl), E (ethyl), P (propyl), Bz (benzyl)) were obtained according to the following general procedure (see ESI† for synthetic details of all compounds).

A Schlenck was charged with the corresponding *N*-monoquaternised quinoxalinium cation [RQ](X) (X$^-$ = I, Br, PF_6) and an excess of sodium dithionite ($Na_2S_2O_4$) in MeOH. The system was purged with nitrogen, closed and agitated in an ultrasound bath for 15 min. Upon standing for 7 d, a purple microcrystalline solid had formed from the dark blue reaction mixture. This was isolated by filtration, copiously-washed with MeOH and water, then dried under vacuum. Electronic and IR spectroscopy as well as elemental analysis have been performed on each samples. Complementary single crystal X-ray diffraction analysis has been also performed only in the case of R = propyl. All the experiments confirm that the purple products correspond to the direduced monoprotonated cationic form **Rbqn^0-H$^+$** (Fig. 1) of the corresponding biquinoxen dications **Rbqn**$^{2+}$, as already known for **Mbqn^0-H$^+$**.[5] Furthermore, the presence of sulfur in each elemental analysis (ESI†) shows that the charge of the organic moieties is at least always partially balanced by some sulfur oxygen containing anions.

In particular, the purple powders exhibit a characteristic broad absorption in the range 200–1400 nm as well as strong IR vibrations in the 1580–1720 cm^{-1} region (ESI†). In all cases these optical and vibrational signatures are in line with the one obtained by studying crystals of **MBqn^0-H$^+$**[BF_4] for which the protonation has been perfectly proved.[5] However, we notice an increase of the IR vibration peak from 1638 to 1695 cm^{-1} as the bulkiness, and probably the twist angle around the central C–C bond, of the R substituent increases from methyl to benzyl (ESI†).

In order to confirm that the purple intermediates correspond to the direduced monoprotonated species **Rbqn^0-H$^+$** a complementary X-ray structure determination has been performed on dark purple crystals in the case of R = propyl and is consistent with the formula [**Pbqn^0-H$^+$**]$_2$($S_4O_6^{2-}$), the **Pbqn^0-H$^+$** species being balanced here by the presence of tetrathionate ion. Although the dataset is reliable, the very small size of the crystal precluded definitive identification of all the H-atoms from Fourier difference maps. However the structure analysis revealed the features characteristic of a direduced monoprotonated species (Fig. 2), as it has been unambiguously described for **Mbqn^0-H$^+$**.[5] In particular, the two crystallographically independent **Pbqn^0-H$^+$** units adopt the typical *cis*-configuration (ϕ = 7.2° and 8.3°) where the dihedral angle is defined as ϕ = C_2–C_3–C_3′–C_2′. Remarkably, compared with **Mbqn^0-H$^+$** (ϕ = 2.5),[5] the larger dihedral angles for **Pbqn^0-H$^+$** confirm that the increase of the length of the R substituent leads to a twist of the molecule around the central C–C bond. Furthermore, monoprotonation induces an asymmetry within the organic moieties as well as between the organic moieties and the tetrathionate ion. As in the case of **Mbqn^0-H$^+$**,[5] but less pronounced, the protonated side of each **Pbqn^0-H$^+$** adopts a rather stiffened quinoid type structure[5] with localised alternating long–short–long N_1′–C_2′,

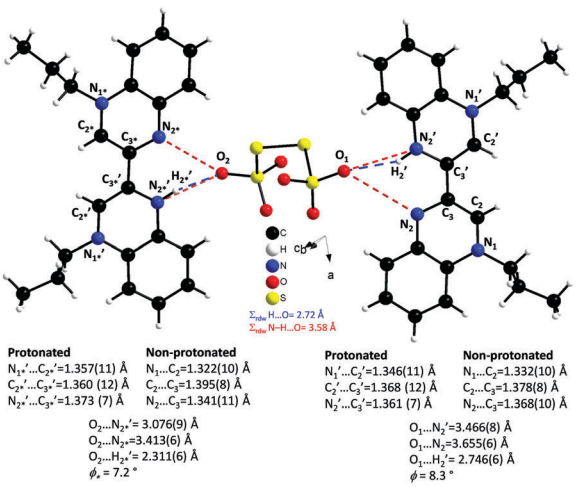

Fig. 2 Ball & Stick view of the asymmetric unit of [**Pbqn^0-H$^+$**]$_2$($S_4O_6^{2-}$). Salient C–C, C–N, O–N, O···H distances and dihedral angle ϕ = C_2–C_3–C_3′–C_2′ are indicated.

C_2'–C_3' and C_3'–C_3 bond distances, respectively. In contrast, the non-protonated side of the molecule is rather aromatic with an opposite short–long–short trend in the corresponding bond distances (Fig. 2). Furthermore, the presence of hydrogen bonds N_2'–H$\cdots O_1$ and $N_{2\star}'$–H$\cdots O_2$ between the H-bond donor atoms (N_2', $N_{2\star}'$) of the organic species and the H-bond acceptor atom (O_1, O_2) of the tetrathionate ion is obvious. Indeed, in the hypothesis of non-protonation of the organic moieties the $N_2\cdots O_1$ and $N_2'\cdots O_1$ interatomic distances (same features for $N_{2\star}\cdots O_2$ and $N_{2\star}'\cdots O_2$) should, in principle, be equal (symmetrical situation with no preferred interactions between the organic species and the tetrathionate). In fact, the $N_2'\cdots O_1$ and $N_{2\star}'\cdots O_2$ distances are much shorter than the $N_2\cdots O_1$ and $N_{2\star}\cdots O_2$ respectively by about 0.19–0.34 Å which is in line with our suggestion that the intermediate purple species with R = propyl is the monoprotonated form **Pbqn^0-H$^+$**.

In order to oxidise the purple solid containing **Rbqn^0-H$^+$**, this was partially dissolved in 1 : 1 DMF/acetic acid mixture and stirred 30 min in air. Any remaining solid was filtered and washed with acetic acid. The resulting dark yellow filtrate was acidified with HBF_4 thus precipitating the *N*,*N*′-diquaternised biquinoxens, [**Rbqn^{2+}**]$(BF_4)_2$, as pale yellow/off-white crystalline salts in yields up to 32%.

Each compound was characterised by ^{1}H and ^{13}C NMR, electronic and IR spectroscopy as well as FAB mass spectrometry. **Mbqn^{2+}**, **Ebqn^{2+}** and **Bzbqn^{2+}** have been also identified by single crystal and powder X-ray diffraction and correspond to [**Mbqn^{2+}**]$(BF_4)_2$·MeCN, [**Ebqn^{2+}**]$(BF_4)_2$ and [**Bzbqn^{2+}**]$(BF_4)_2$·2MeCN, respectively. Crystals of **Pbqn^{2+}** were heavily twinned precluding any structure determination.

Possible mechanism

Under anaerobic conditions the reaction of the *N*-alkylquinoxalinium cation with dithionite gives a dark blue solution accompanied by the formation of the *N*,*N*′-diquaternised biquinoxens, first isolated in their intermediate cationic di-reduced monoprotonated forms. These features are in line with an oxidative radical homocoupling between two chemically reduced *N*-alkylquinoxalinium rings, as suggested by Chupakhin *et al.* when studying quinoxaline ring dimerisation (Fig. 3).[7,12] In their proposed mechanism, by monoprotonating the quinoxaline the carbon alpha to the ammonium function becomes sufficiently electron deficient for a subsequent nucleophilic substitution of the hydrogen in the aromatic system. When the reaction is carried out under an inert atmosphere, the homolytic σ-decomposition of the intermediate species leads to the formation of a 1,4-dihydroquinoxalinyl radical cation, which subsequently couples to give the biquinoxalinium species after oxidation.[7,12]

In our system, we propose a similar mechanism involving the *N*-alkyl-4-hydroquinoxalinyl radical cation as a key intermediate (Fig. 3). The *N*-alkylquinoxalinium cation is first reduced by sodium dithionite ($Na_2S_2O_4$). This is known to proceed *via* two different mechanisms.[13] Here, one possibility involves the

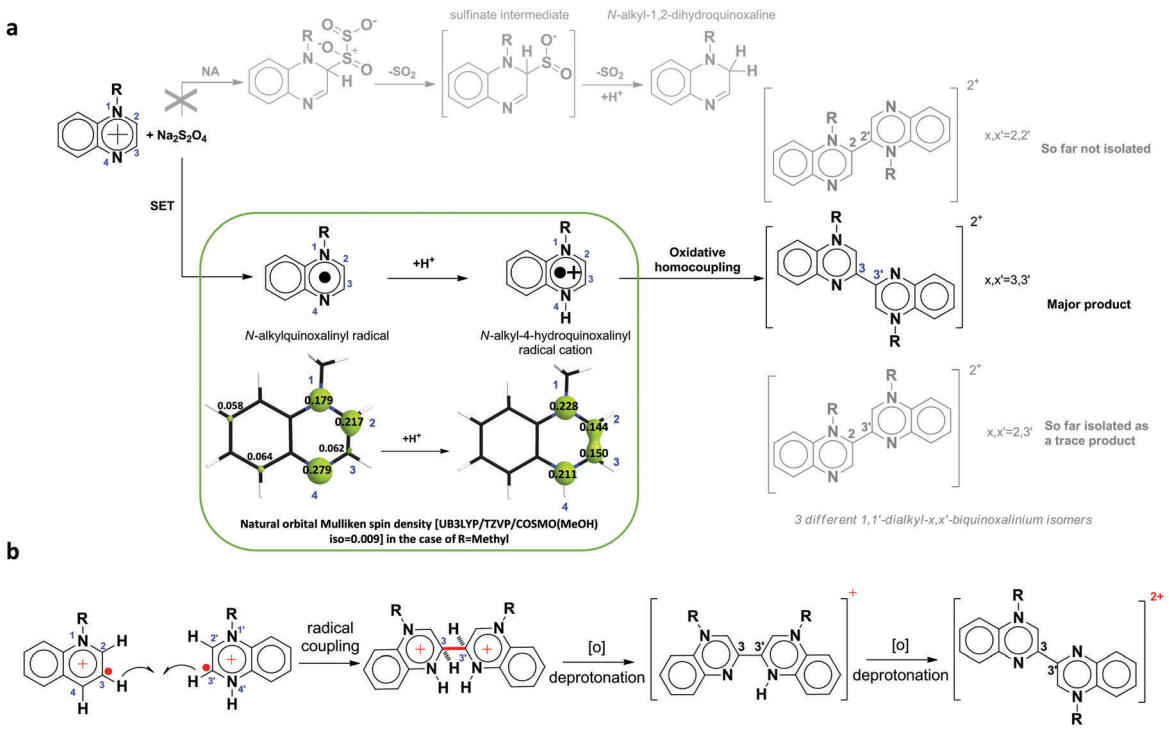

Fig. 3 Proposed mechanism of oxidative radical homocoupling for the synthesis of *N*,*N*′-diquaternised biquinoxen dications **Rbqn^{2+}** (R = Me, Et, Pr, Bz). (a) A single electron transfer (SET) occurs between dithionite ($S_2O_4^{2-}$) and a *N*-alkylquinoxalinium cation leading to a *N*-alkylquinoxalinyl radical. Subsequent protonation gives the *N*-alkyl-4-hydroquinoxalinyl radical cation, which after oxidative homocoupling gives the *N*,*N*′-dialkyl-3,3′-biquinoxalinium **Rbqn^{2+}** isomers as the major product. (b) Scheme of the radical homocoupling followed by partial oxidation of the *x*,*x*′ = 3,3′ isomer, leading to the stable intermediates **Rbqn^0-H$^+$** which by complete oxidation give the *N*,*N*′-diquaternised biquinoxen dications, **Rbqn^{2+}**.

nucleophilic addition (NA) of the $S_2O_4^{2-}$ anion on the carbon alpha to the ammonium function (C_2) to form the sulfinate intermediate, which would then be reduced to the *N*-methyl-1,2-dihydroquinoxaline species by loss of SO_2 (Fig. 3a). So far such a reduced species could not be identified in our experiments. The second reduction mechanism involves only a single electron transfer (SET) from the dithionite to the *N*-alkylquinoxalinium cation leading to the *N*-alkylquinoxalinyl radical (Fig. 3a). In fact, we favour this SET from dithionite since it is a common technique used to generate radical species of *N*-substituted electron deficient cationic heterocycles.[14–16]

EPR spectroscopy

The SET mechanism leads to the formation of an *N*-alkyl-4-hydroquinoxalinyl radical as we confirmed by EPR spectroscopy. Reduction of *N*-methylquinoxalinium with $Na_2S_2O_4$ in MeOH, DMF or DMSO results in the immediate formation of a dark plum reaction mixture characterised by a multiline EPR spectrum in all cases (Fig. 4). The signal is consistent with an $S = 1/2$ *N*-alkyl-4-hydroquinoxalinyl whose rich hyperfine pattern stems from the inequivalence of its eight protons (^1H, $I = 1/2$, ~100% abundant) and two nitrogens (^{14}N, $I = 1$, ~100% abundant). However, EPR is not able to differentiate between hydroquinoxalinyl and quinoxalinyl radical forms unlike in the more symmetric pyrazinyl analogue that gave a less dense splitting profile which confirmed the presence of the protonated species. Nevertheless, this signal is in stark contrast to the reduced homocoupled product, **MBqn$^{\bullet+}$-H$^+$**,[5] which gives its signature 9-line spectrum in DMF and DMSO solution (Fig. 4). The most realistic scenario is that the radical is protonated in solution since as is commonly observed when reducing similar *N*-mono-quaternised cationic 1,4-diazine heterocycles with dithionite such as *N*-methylpyrazinium.[14,17–19]

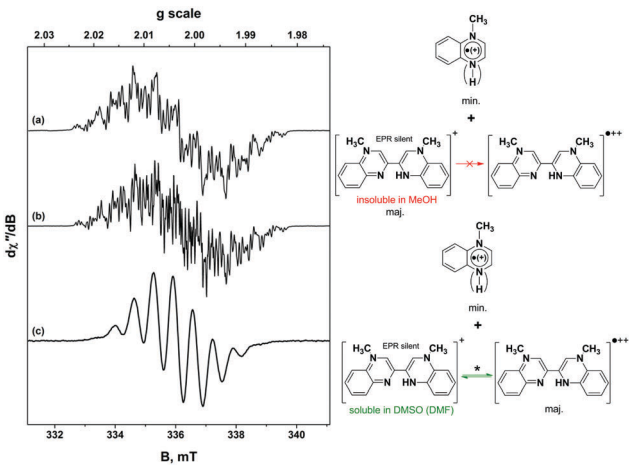

Fig. 4 (left) Comparison of the X-band EPR spectra obtained from the reduction of *N*-methylquinoxalinium iodide: (a) in methanol; (b) in DMSO after 30 min; (c) in DMSO after 24 h. Experimental conditions: frequency, 9.423 GHz; modulation, 0.05 mT; power, 20 mW. (right) Scheme representing the relationship between the EPR signals and the different species in presence after 24 h of reaction in MeOH (top) and DMSO (bottom). *Features already observed in ref. 5.

To explore this further we compared the spin density distribution of the *N*-alkyl-4-hydroquinoxalinyl radical and the corresponding radical cation in solution (B3LYP/TZVP/COSMO level of theory). We especially focused on R = Me, *i.e.* the *N*-methyl-4-hydroquinoxalinyl radical and corresponding radical cation, using the structural parameters of the simple *N*-methylquinoxalinium cation.[20] The behaviour of the other *N*-quaternised quinoxalinium salts are most probably identical. As shown in the inset of Fig. 3a the spin density of the neutral *N*-methyl-quinoxalinyl radical is mostly located on the atoms N_1, N_4 and C_2. As reported for other radical coupling reactions,[21] the nearly zero spin density on C_3 cannot explain a direct or at least efficient radical coupling between two C_3 atoms, which is however observed experimentally through the formation of the central C_3–C_3' sigma bond in both the organic species **Rbqn^0-H$^+$** and **Rbqn^{2+}**. In contrast, the protonation of the *N*-methylquinoxalinyl radical giving the *N*-methyl-4-hydroquinoxalinyl radical cation (Fig. 3a, inset) results in a better distribution of the spin density on C_3 which definitely favours such a radical coupling between two C_3 atoms.

Regioselectivity aspects

The symmetric nature of the 1,4-dihydroquinoxalinyl radical cation studied by Chupakhin *et al.* leads to a single biquinoxalinium product after oxidative radical coupling.[7,12] In contrast, due to the asymmetric nature of the *N*-alkyl-4-hydroquinoxalinyl radical cation and the fact that the spin density on both C_2 and C_3 carbons is essentially the same, the oxidative radical coupling should be, in principle, non regioselective. Although this should theoretically give three different *N*,*N*′-dialkyl-*x*,*x*′-biquinoxalinium isomers (abbreviated as *x*,*x*′), depending on which carbon atoms form the central bond (isomers *x*,*x*′ = 2,2′, 2,3′ or 3,3′ – Fig. 3a), this will depend on the chemical stability of the species towards oxidation and/or to the possibility to isolate these through fractional crystallisation. So far, the *x*,*x*′ = 2,2′ isomer has not been isolated, while a single crystal of an *x*,*x*′ = 2,3′ isomer – *N*,*N*′-diethyl-2,3′-biquinoxalinium – has been obtained only in its fully oxidised dicationic form under reducing conditions. In contrast, the *x*,*x*′ = 3,3′ isomers are systematically isolable in their partly oxidised form **Rbqn^0-H$^+$**, thus giving pure phases of **Rbqn^{2+}** after a simple aerial oxidation step. In short, although the disadvantage is that the coupling reaction is not regioselective, which might explain a maximum yield limited to 1/3 (1 isomer over 3; maximum yield of 32% observed (ESI†)), the huge advantage is that the 3,3′-isomers "biquinoxens" are easily isolable without any further purification step.

As a possible explanation for why it is possible only to crystallise the *x* = 3,3′ species from the intermediate step, from our experience on **Mbqn^0-H^{+5}** as well as from previous investigations on the effect of steric hindrance in radical coupling reactions[22,23] and on the ease of reduction, *i.e.* radical stability, of geometrically restrained viologens,[24] all indicate that the *x*,*x*′ = 3,3′ isomer is the only form which can be stabilised in solution in its reduced state compared with *x*,*x*′ = 2,2′ and 2,3′. This is in part due to the stabilising factors of perfect planarity of the molecule and a full π-electron delocalisation. These are

in line with the most stable configuration of the direduced species where the π-electron density is paired on the central C_3–C_3' bond.[5] In the case of *x*,*x*′ = 2,2′ and 2,3′ the fact that a more sterically hindered C_2 atom is involved can strongly disfavour the coupling reaction[22,23] and/or decrease the radical stability of the direduced species by inducing a significant twist of the molecule around the central C_2–C_2'(C_3') bond.[24]

Furthermore, the insolubility of the *x*,*x*′ = 3,3′ isomers **Rbqn^0-H$^+$** in MeOH greatly enhances the yield of the reaction compared to other solvents. As mentioned above, EPR confirmed the observation of the *N*-alkyl-4-hydroquinoxalinyl radical species (ESI†) in MeOH, DMF and DMSO with a qualitative rate of colour change of the solution to dark blue (radical formation) increasing in the order MeOH < DMF < DMSO, which is in line with a better solubility of sodium dithionite in DMSO rather than in MeOH (Fig. 4). However, as already known for **Mbqn^0-H^{+5}** the much better solubility of **Rbqn^0-H$^+$** in DMF or DMSO precludes precipitation of the **Rbqn^0-H$^+$** form which remains in solution in equilibrium with the corresponding radical **Rbqn$^{\bullet+}$-H$^+$**. Thus, this explains the non-measurable yields reported using DMF or DMSO solvents, the best yields being exclusively obtained in MeOH.

Counter ion influence on yield

The influence of the anion on the reaction yield has also been investigated (ESI†). It is clear that the counter ion plays a significant role with an increase in the yield of the [**Rbqn^{2+}**]$(BF_4)_2$ species (R = methyl, ethyl and benzyl) from 9% to 32% in the order of starting anions I^- < Br^- < PF_6^-. This is in line with the fact that I^- ions are more oxidisable and have a higher degree of ion pairing compared to Br^- and also PF_6^- ions. This favours quenching reactions involving iodide-mediated charge/electron transfer or radical scavenging mechanisms.[25–28]

However, the low yields observed in the case of R = propyl, either starting from I^- or PF_6^-, suggest that the isolation of the [**Rbqn^{2+}**]$(BF_4)_2$ species also depends on the intrinsic solubility of the biquinoxen dications which in turn is governed by the type of R substituent.

Further experiments will be performed in future investigating these aspects in order to optimise the yields of the reactions.

Conclusions

In conclusion we have reported the oxidative radical homocoupling of chemically reduced *N*-alkylquinoxalinium salts as an alternative method for the synthesis of *N*,*N*′-diquaternised-3,3′-biquinoxalinium ''biquinoxens'' dications. Although referring back to Fig. 1 it is clear that left hand route can provide much better yields. This critically relies on the availability of the corresponding oxonium derivatives. The right hand route, despite non regioselectivity, still provides yields of up to 32%. Since this method is very simple it allows for gram scale synthesis at room temperature whilst using inexpensive reagents, no metal catalysts and no purification steps. Furthermore, the chemistry of the quinoxaline quaternary salts used here is more accessible than that of biquinoxaline, the previously reported starting reagent. This provides exciting prospects for simple access to new members of the biquinoxen family bearing various electron withdrawing/donating and possibly chiral groups as well as coordination functions.

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