RSC Advances

Unsubstituted Quinoidal Pyrrole and its Reaction with Oxygen, Charge Transfer and Palladium(II) Complexes via DDQ Oxidation

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Abstract

The dehydrogenation reaction of 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) followed by treatment with sodium bicarbonate afforded two new products containing oxygen atoms, 2,5-bis(3,5-dimethylpyrazolylcarbonyl)pyrrole (**2**) and 5-{bis-(3,5-dimethylpyrazolyl)methyl}pyrrole-2-carbaldehyde (**3**). Interestingly, the products are different when the reaction mixture was not treated with base, which are **2**, 2-tri(3,5-dimethylpyrazolylmethyl)-5-(3,5-dimethylpyrazolylcarbonyl)pyrrole (**4**) and the adduct **5**, the 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$) adduct of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole (**6**) isolated in 22% yield in which **6** acts as an electron acceptor and $DDQH_2$ as an electron donor. The treatment of **5** with $NaBH_4$ or basic alumina afforded the free base **6** in good yield, representing the discrete unsubstituted quinoidal structure of pyrrole. **6** is fluorescent, reactive and could have its biradical resonance structure as demonstrated by its reaction with dioxygen only under the irradiation of sunlight, otherwise not reacting, giving the oxygen containing products: **2**, bis-(3,5-dimethylpyrazolyl)methanone (**7**) and 2-(3,5-dimethylpyrazolylcarbonyl)-5-(3,5-dimethylpyrazolyl)pyrrole (**8**). Further, the quinoidal molecule loses its fluorescene property upon coordination with the palladium metal atom and

gave the binuclear complex, $[Pd_2Cl_4\{\mu\text{-}C_4H_3N\text{-}2,5\text{-}(C(Me_2pz)_2)_2\text{-}N,N,N,N\}]$, in good yield. The structures of most of the compounds including this palladium complex were determined by single crystal X-ray diffraction studies.

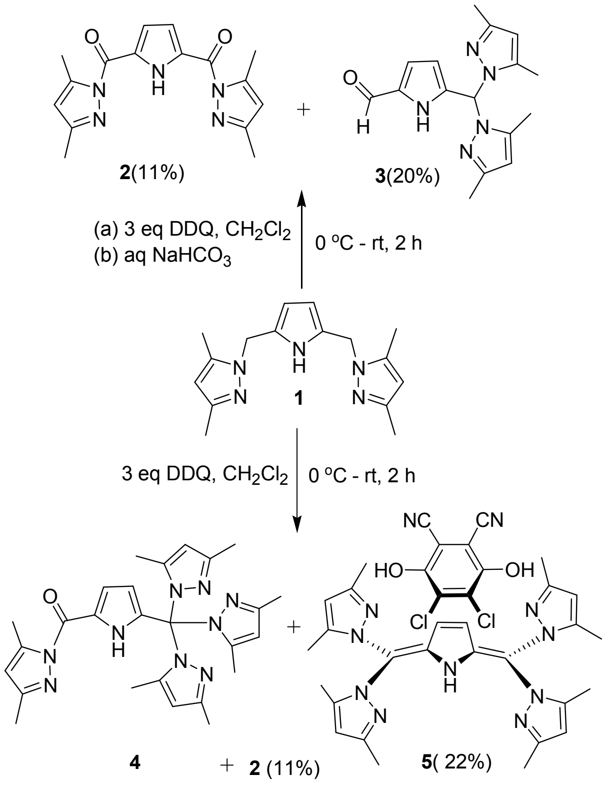
Introduction

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a familiar powerful oxidizing agent used in organic synthesis; it is mainly used for dehydrogenation of hydroaromatic compounds.[1] Besides, DDQ was used to effect the dehydrogenative C–C coupling leading to interesting products,[2] photocatalytic oxygenation of benzene to phenol,[3] and for preparing expanded porphyrins[4] and other π-conjugated molecules.[5] Dolphin and co-workers have reported DDQ oxidation of tripyrrane[6] and dipyrromethane[7] to give unexpected interesting products having extended π-conjugation.[8] As part of our ongoing activity in developing pyrrole-based anion receptors and ligand systems, we became interested to oxidize 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole[9] **1** with DDQ to give conjugated molecules, as **1** possesses two methylene groups. Herein we report the reactive, fluorescent and π-conjugated quinoidal form of simple pyrrole, which forms the donor-acceptor complex and reacts with oxygen only under sunlight, and the other rearranged oxidation products together with the binuclear palladium complex whose structures were determined by X-ray diffraction.

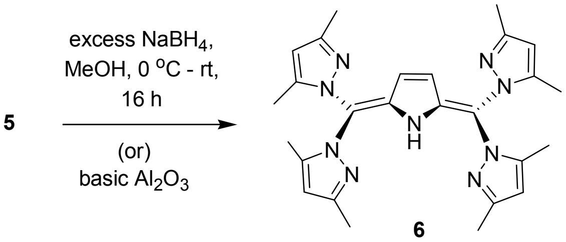
Results and Discussion

As shown in Scheme 1, the oxidation reaction of 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole **1** with three equiv of DDQ followed by treatment with a base ($NaHCO_3$) afforded the two new products **2** and **3** in 11% and 20% yields, respectively, after silica gel column chromatography separation. On the other hand, the same reaction without treatment with a base afforded the 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$) adduct **5** in 22% yield, in addition to **2** formed in 11% yield and **4** in very low yield as yellow coloured crystals after silica gel column chromatographic separation. Presumably, in the presence of sodium bicarbonate, the adduct **5** disintegrates into its components and the liberated quinoidal pyrrole molecule, 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6**, then underwent further reactions with air probably during work-up procedure to give **2**–**4** containing oxygen atoms. Therefore, it is likely in both reactions, the free quinoidal pyrrole molecule **6** (see below) initially might have formed which then reacts to the by-product of the reaction, DDQH$_2$, to give the adduct **5** in which **6** can act as an electron acceptor and DDQH$_2$ as an electron donor. However, this reaction did not give the expected molecule, that is, molecule containing one pyrrole ring flanked by two pyrazolylmethylene groups with π conjugation, probably because of the reaction conditions resulting from the presence of three equiv of DDQ and the quite reactive nature of the free base **6** with molecular oxygen (see below).

Scheme 1. The DDQ oxidation products of 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole **1**.



Scheme 2. The generation of the free quinoidal pyrrole molecule **6** from the adduct **5**.



In consistent with the reaction products obtained with sodium bicarbonate, the treatment of the DDQH$_2$ adduct **5** with another base NaBH$_4$ afforded the free base **6** in 67% yield. In addition, **6** was also obtained after passing the adduct **5** through a basic alumina column (Scheme 2). All these oxidized products are soluble in common organic solvents such as diethyl ether, toluene and chloroform and their structures were confirmed by X-ray diffraction studies.

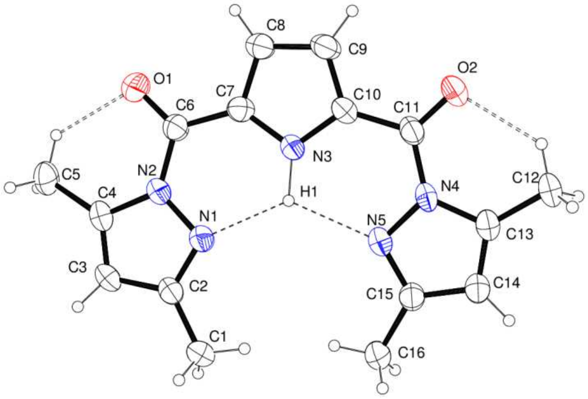


Fig. 1 Molecular structure of **2** (30% thermal ellipsoids): Dotted lines indicate hydrogen bonds. Selected bond lengths (Å) and angles (deg): N1–N2 1.376(5), N2–C6 1.407(5), C6–O1 1.220(5), C6–C7 1.458(6), N3–C7 1.361(5), C7–C8 1.388(6), C8–C9 1.383(7), C9–C10 1.376(6), N3–C10 1.356(5), C10–C11 1.470(6), C11–O2 1.212(5), N4–C11 1.410(5), N4–N5 1.370(5), O1–C6–N2 119.0(4), O1–C6–C7 120.2(4), O2–C11–N4 120.1(4), O2–C11–C10 120.4(4), N1–N2–C6 120.8(3), C7–N3–C10 109.0(4), N5–N4–C11 121.3(3), N2–C6–C7 120.7(4), N3–C10–C11 128.3(4), C10–C11–N4 119.5(4), N3···N1 2.738(5), H1···N1 2.03(5), N3–H1···N1 118(3), N3···N5 2.706(5), H1···N5 2.11(4), N3–H1···N5 110(3),

C5⋯O1 2.824(6), H5a⋯O1 2.09, C5–H5a⋯O1 131.8, C12⋯O2 2.819(6), H12a⋯O2 2.09, C12–H12a⋯O2 131.6.

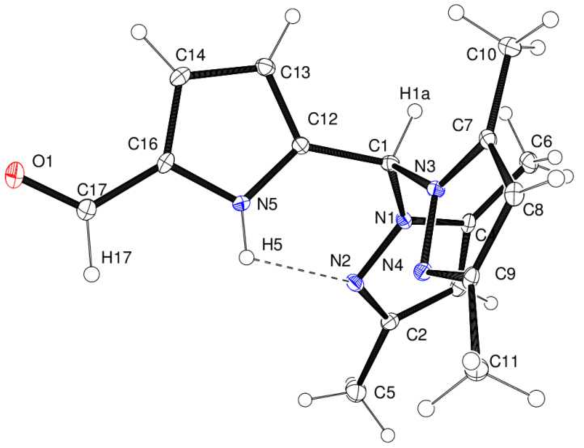


Fig. 2 Molecular structure of **3** (30% thermal ellipsoids): Dotted lines indicate hydrogen bond. Selected bond lengths (Å) and angles (deg): O1–C17 1.2207(19), C16–C17 1.445(2), C14–C16 1.381(2), C13–C14 1.398(2), C12–C13 1.380(2), N5–C16 1.378(2), N5–C12 1.358(2), C1–C12 1.500(2), N1–C1 1.442(2), N3–C1 1.466(2), O1–C17–C16 123.7(2), N5–C16–C17 121.8(2), C12–N5–C16 109.0(1), N5–C12–C1 125.4(2), N1–C1–C12 115.3(1), N3–C1–C12 111.4(1), N5⋯N2 2.921(2), H5⋯N2 2.49(2), N5–H5⋯N2 111(1).

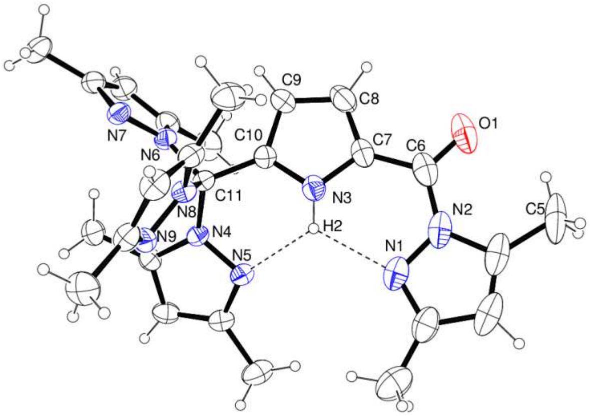


Fig. 3 Molecular structure of **4**: Dotted lines indicate hydrogen bonds. Selected bond lengths (Å) and angles (deg): C6–O1 1.204(7), C6–N2 1.415(8), C6–C7 1.464(8), C7–C8 1.365(8), C7–N3 1.369(6), C8–C9 1.385(7), C9–C10 1.382(7), C10–N3 1.359(6), C10–C11 1.505(7), C11–N4 1.462(6), C11–N6 1.471(6), C11–N8 1.472(6), O1–C6–N2 119.7(6), O1–C6–C7

121.2(7), N2–C6–C7 119.1(6), N3–C7–C6 127.5(6), N3–C10–C11 123.3(4), N4–C11–N6 107.5(4), N4–C11–N8 107.1(4), N6–C11–N8 110.2(4), N4–C11–C10 113.2(4), N6–C11–C10 107.8(4), N8–C11–C10 111.0(4), N3···N1 2.682(7), H2···N1 2.13(5), N3–H2···N1 118(4), N3···N5 2.739(6), H2···N5 2.18(5), N3–H2···N5 119(4).

The X-ray structures of **2-4** (Fig. 1, Fig. 2 and Fig. 3, respectively) revealed the presence of carbonyl group together with the rearranged pyrazolate groups attached to the α-positions of the pyrrole ring. The presence of carbonyl group indicates that these products could have formed by the reaction of the initially formed quinoidal pyrrole molecule **6** with air. A complete planar conformation was observed for **2**, whereas in the cases of **3** and **4**, the planarity is maintained in the carbonyl group side of the molecule which consists of the pyrrole ring and the aldehyde (**3**) or 3,5-dimethylpyrazolylcarbonyl group (**4**). This planarity indicates the presence of extended π-conjugation among these groups. Further, in the structures of **2** and **4**, the acidic pyrrolic NH group forms the three centre hydrogen bond[10] with the pyrazolyl nitrogen atoms. Probably because of these hydrogen bonds, the two carbonyl groups in **2** are oriented in one direction. This is in contrast to the thiophene based molecule which exhibits its carbonyl groups oriented opposite to each other.[11] The ^{1}H NMR spectra of **2** and **4** in $CDCl_3$ showed resonances in a fairly deshielded region at δ 13.00 ppm and 12.04 ppm, respectively, for their pyrrolic NH protons probably because of the three centre hydrogen bonding interactions in these molecules. Conversely, the structure of **3** showed one intramolecular hydrogen bond between the pyrrolic NH and the adjacent pyrazolyl nitrogen atom; the NH group resonates at 10.74 ppm in the ^{1}H NMR spectrum.

The adduct **5** is a fluorescent yellow coloured solid and gives absorption maxima at 421 nm and 442 nm, and an emission maximum at 490 nm after excitation carried out at 420 nm in DMSO (see ESI, Fig. S25a). Its fluorescent property could originate from the π-electrons involved in conjugation. The ^{13}C NMR spectrum of **5** in $CDCl_3$ shows 17 peaks including resonances due to $DDQH_2$ as expected for this complex. These chemical shift values shifted only slightly to both the deshielded and shielded regions with respect to those of the free base **6** (see below). On the other hand, ^1H NMR spectrum of **5** shows noticeable changes for the resonances due to the methyl and the pyrrolic NH protons, suggesting that the complex is not dissociated and the solid state structure of **5** (see below) is preserved in $CDCl_3$ solution. Conversely, the ^1H NMR of **5** in DMSO-d_6 (see ESI, Fig. S10) shows the spectral pattern very close to that of the free base **6** in DMSO-d_6 (see ESI, Fig. S12). This suggests that the charge transfer complex **5** dissociates into its component molecules in Lewis base solvent DMSO. This is also supported by the UV-vis spectrum of a dilute solution of **5** in DMSO which appears to be very close to that of the free base **6.** Conversely, the same charge transfer complex in toluene (see ESI, Fig. S26) displays a discrete absorption band λ_{max} at 353 nm, in addition to absorbances at 424 nm and 444 nm. The absorption at 353 nm (80.1 kcal/mol) can be regarded as the charge transfer band for this compelx, which is in the order of shorter wavelength charge transfer band values reported for pyridinium iodides.[12] A dichloromethane solution of **5** also gives a similar UV-vis spectrum. The observation of the charge transfer band in toluene or dichloromethane indicates that the complex **5** is not dissociated in these solvents. In addition, the solid state UV-vis spectrum of **5** (see ESI, Fig. S28) exhibits rather broad band in the same region where the absorptions are observed in the solution state spectra. Furthermore, in support of the presence of the benzenoid system of $DDQH_2$ in **5,** the FTIR spectrum contains bands at 3222 cm^{-1} and 2251 cm^{-1} due to the ν(OH) and ν(CN) stretching frequencies, respectively, which is confirmed by X-ray structure.

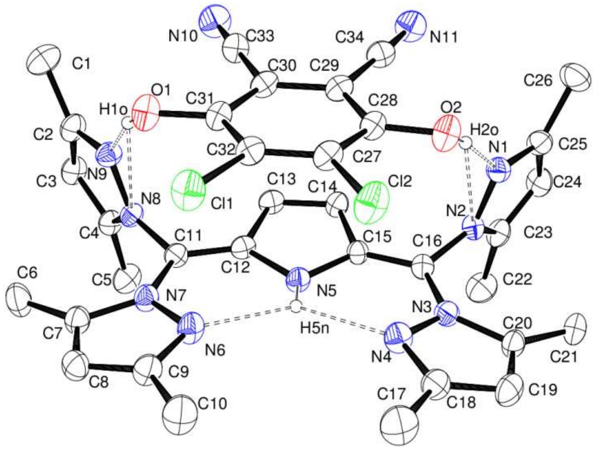


Fig. 4 Molecular structure of **5** (30% thermal ellipsoids). Most hydrogen atoms are omitted for clarity. Dotted lines indicate hydrogen bonds. Selected bond lengths (Å) and angles (deg): N6–N7 1.373(4), C11–N7 1.409(5), C11–N8 1.411(5), N8–N9 1.379(4), C11–C12 1.353(6), C12–N5 1.387(5), C12–C13 1.448(6), C13–C14 1.339(6), C14–C15 1.448(5), C15–N5 1.380(5), C15–C16 1.345(5), C16–N2 1.416(5), C16–N3 1.411(5), N1–N2 1.379(5), N3–N4 1.373(5), C31–O1 1.345(5), C28–O2 1.339(5), C31–C32 1.407(6), C30–C31 1.383(6), C27–C32 1.381(6), C27–C28 1.394(6), C28–C29 1.389(5), C29–C30 1.420(6), C32–Cl1 1.717(4), C27–Cl2 1.723(4), C29–C34 1.440(6), C34–N11 1.143(5), C30–C33 1.447(6), C33–N10 1.132(5), N7–C11–N8 116.4(4), C12–C11–N7 124.8(4), C12–C11–N8 118.4(4), C11–C12–N5 128.1(4), C15–N5–C12 110.9(3), C16–C15–N5 128.6(4), C15–C16–N3 126.4(4), C15–C16–N2 117.8(4), N5···N6 2.730(5), H5n···N6 2.21(4), N5–H5n···N6 120(4), N5···N4 2.801(5), H5n···N4 2.28(4), N5–H5n···N4 121(4), O1···N9 2.635(5), H1o···N9 1.65(5), O1–H1o···N9 168(4), O2···N1 2.688(5), H2o···N1 1.77(5), O2–H2o···N1 173(4), C12···C31 = 3.5930(2), C13···C30 = 3.4644(2), C14···C29 = 3.4721(2), C15···C28 = 3.5923(2).

Complex **5** crystallizes in the triclinic space group *P*-1. The free base **6** and one molecule of DDQH$_2$ constitute the asymmetric unit representing the adduct formation as shown in Fig.

4. The $DDQH_2$ C–C (1.381(6) to 1.420(6) Å) and C–O (1.339(5) Å and 1.345(5) Å) bond distances suggests the presence of partial double bond character and the benzenoid system, not quinoid. These distances are similar to the benzenoid systems in other reported charge transfer complexes.[13] Hence, the free base **6** acts as an electron-acceptor and $DDQH_2$ acts as an electron-donor in complex **5**.

In contrast to the free base structure **6** in which all pyrazolate rings are twisted with respect to the pyrrole ring plane (see below), two of the pyrazole rings one from each side in **5** are almost coplanar to the pyrrole ring plane which is parallel to that formed by $DDQH_2$, This parallel arrangement and the inter planar (C···C) distances indicate that there can be some π-π interaction. Conversely, the nitrogen atoms of the other two perpendicularly oriented pyrazole rings with the dihedral angle N1–N2–C16–C15 = 93.5(5)° are hydrogen bonded to $DDQH_2$. However, all the pyrazolate nitrogen-methylene carbon bond distances are almost the same and range from 1.409(5) to 1.416(5) Å. Further, these distances are shorter than those single bond distances [1.473(6) Å and 1.466(5) Å] found in the structure of 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole **1**, indicating the involvement of pyrazolate groups in the extended π-conjugation. The bond distances, C14–C15 = 1.448(5) Å and C12–C13 = 1.448(6) Å, refers to single bonds which are longer than the alternatively located double bonds distances (C11–C12 = 1.353(6) Å, C13–C14 = 1.339(6) Å and C15–C16 = 1.345(5) Å), supporting the quinoidal pyrrole structure. Upon comparison to the free base **6**, a noticeable change is observed for the pyrrole ring C–C double bond distance (1.339(6) Å (**5**) and 1.363(10) Å (**6**)). These metric parameters changes are attributed to the interaction between the quinoidal pyrrole and $DDQH_2$. The pyrrolic NH proton forms three-centred hydrogen bonds with the nitrogen atoms of the pyrazolate rings located in front of it.

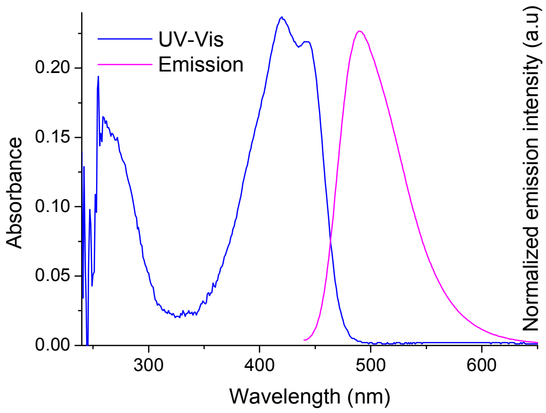


Fig. 5 UV-Vis and emission (490 nm) spectra of the quinoidal pyrrole molecule **6** in DMSO (10^{-5} M).

Compound **6** is a yellow coloured solid and stable in air, but decomposes in solution under sunlight. Its emission (490 nm) and absorption (421 nm and 443 nm) spectra are very close to that of **5** in DMSO with 0.023 quantum yield (Fig. 5). The ^{1}H NMR spectrum of **6** in $CDCl_3$ features the pattern of signals resembling that of **5**. However, the characteristic signal is the resonance due to the pyrrolic NH proton at δ 9.42 ppm, which is in the slightly shielded region in comparison to that of the adduct **5** (δ 9.64 ppm), among other chemical shift changes. The ^{13}C NMR spectrum shows only 13 number of peaks, which is in accord with the X-ray structure.

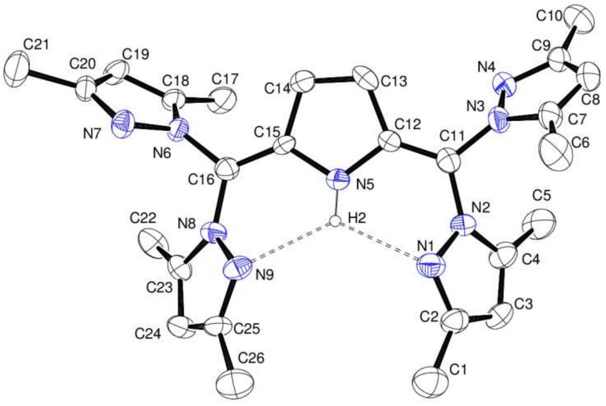
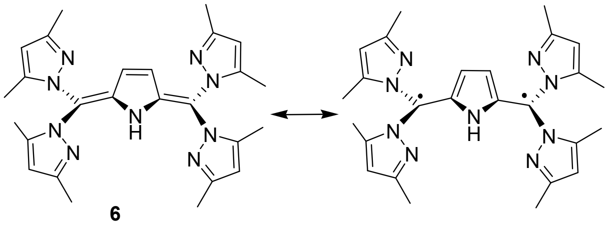


Fig. 6 Molecular structure of **6** (30% thermal ellipsoids): Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C11–C12 1.335(10), C11–N3 1.413(9), C11–N2 1.425(9), C12–N5 1.392(9), C12–C13 1.451(10), C13–C14 1.363(10),

C14–C15 1.426(9), C15–C16 1.362(10), C15–N5 1.387(8), C16–N6 1.414(9), C16–N8 1.407(9), C12–C11–N3 122.6(7), C12–C11–N2 121.5(7), N3–C11–N2 115.9(7), C11–C12–N5 125.0(7), C11–C12–C13 129.6(7), C16–C15–N5 125.3(6), C16–C15–C14 128.5(7), C15–C16–N6 120.2(6), C15–C16–N8 122.3(7), N6–C16–N8 117.4(7), N5···N9 2.885(5), H2···N9 2.30(7), N5–H2···N9 121(5), N14···N15 2.873(8), H1···N15 2.33(7), N14–H1···N15 123(6).

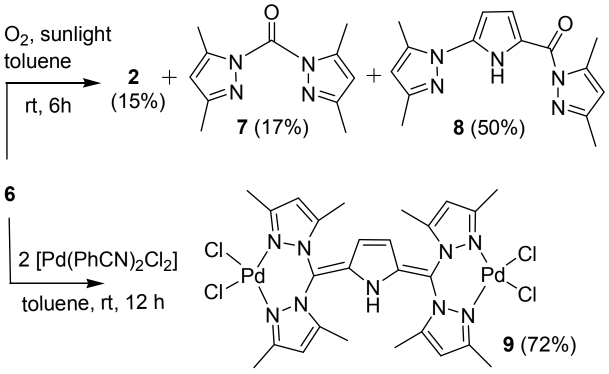
Compound **6** crystallizes in the orthorhombic space group *Pna*2_1 and two molecules of **6** constitute the asymmetric unit. These two independent molecules have almost identical metric parameters and an ORTEP view of one of the molecules is shown in Fig. 6. In contrast to the structure of **5**, the X-ray structure of the free base **6** adopts a different conformation in which none of the pyrazole rings are coplanar to the pyrrole ring plane, but the pyrazolate nitrogen atoms (N2, N3, N6 and N8) bonded to the methylene carbons are in the plane defined by the pyrrole ring together with the methylene carbon atoms (C16 and C11). This suggests these pyrazolate nitrogen atoms are involved in the π-conjugation, as was the case in **5**. The other structural features are close to those observed in the adduct structure **5** and the structure represents a novel discrete quinoidal form of pyrrole with NH proton retained, in contrast to N-substituted[14] and fused quinoidal pyrrole ring[15] molecules.



6

Chart A. The proposed biradical resonance structure for the quinoidal pyrrole molecule **6**.

Scheme 3. The reaction of the quinoidal pyrrole molecule **6** with dioxygen under sunlight irradiation and its binuclear palladium(II) complex synthesis.



Molecule **6** is analogous to the thiophene-based quinoidal molecules such as 2,5-dimethylene-2,5-dihydrothiophene and its furan and *N*-methylpyrrole derivatives which have π-conjugations.[16] Interestingly, quinoidal thiophene molecules,[17] Thiele's *p*-xylylene and Chichibabin's hydrocarbons[18] and several other conjugated molecules[19] have been reported to form charge transfer complexes, and shown to exhibit biradical structures and react with molecular oxygen. Having mentioned these, **6** could have the biradical canonical structure, as depicted in Chart A, contributing to the ground state structure. However, the alkenyl-pyrrole carbon distances (C11–C12 = 1.335(10) Å and C15–C16 = 1.362(10) Å) are not elongated considerably; elongation is expected if this biradical canonical structure contributes to the ground state. Nevertheless, the biradical form of **6** could be transient and very reactive. Accordingly, a toluene solution of **6** readily reacts to molecular oxygen O_2 under sunlight irradiation (Scheme 3) to give **7** and **8** along with the dicarbonyl compound **2**, which were separated by silica gel column chromatographic method. Interestingly, no reaction was observed when the toluene solution was exposed to sunlight (visible light) for hours under nitrogen atmosphere, suggesting that the observed products **2-4, 7** and **8**, are the results of the reaction of **6** with air. Further, importantly the reaction between **6** and O_2 did not proceed to completion in the absence of exposure to visible light, that is, in darkness. These observations led us to propose that the transient and reactive biradical species or the excited state structure of **6** could have probably formed *in-situ* upon exposure to the visible light, which then reacts with O_2 or air and cleave the double bond of O_2 to give the oxygen containing products as shown in Scheme 1 and Scheme 3. All compounds but **7** are new compounds. The structure of **8** is based on the spectroscopic data including HRMS(ESI+) which showed the molecular ion [M + H^+] peak at *m/z* 284.1581 (Calc. 284.1511). Its ^{1}H NMR spectrum showed a broad resonance at δ 8.85 ppm for the pyrrolic NH protons. Each of the β-CH proton of the pyrrole ring gives one doublet of doublet and the two different pyrazole CH protons give two separate resonances, which are consistent with the structure. The presence of carbonyl group is confirmed by IR spectrum which displays the ν(CO) stretching frequency at 1700 cm^{-1}.

In addition, a preliminary study of coordination behaviour of **6** was carried out with palladium metal. The reaction of the quinoidal pyrrole **6** with $[Pd(PhCN)_2Cl_2]$ gave the bischelate complex **9** in 72% yield (Scheme 3). Interestingly, upon complexation the fluorescence of **6** is quenched, suggesting that the pyrazole π-electrons are involved in the origin of the fluorescence. The UV-vis absorption spectrum of **9** in acetonitrile showed a blue shifted λ_{max} at 371 nm (ε = 32400 $M^{-1}cm^{-1}$) as compared with that of **6** (Fig. S27).

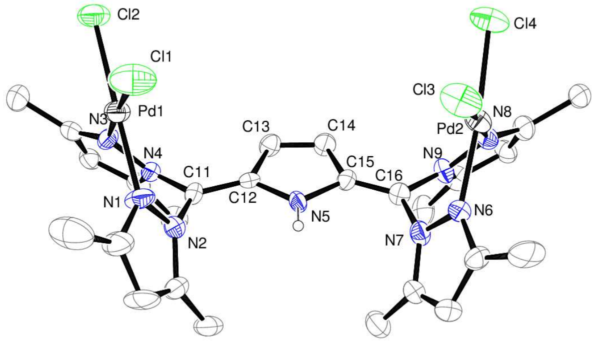


Fig. 7 Molecular structure of **9** with 30% probability ellipsoids. Most hydrogen atoms, acetonitrile and water molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–Pd1 2.020(11), N3–Pd1 2.031(13), Cl1–Pd1 2.284(5), Cl2–Pd1 2.281(4), N6–Pd2 2.039(11), N8–Pd2 2.025(12), Cl3–Pd2 2.273(4), Cl4–Pd2 2.285(4), C11–C12 1.360(18), C11–N2 1.410(17), C11–N4 1.418(18), C12–N5 1.382(17), C12–C13 1.455(18), C13–C14

1.317(19), C14–C15 1.446(18), C15–C16 1.297(18), C15–N5 1.404(16), C16–N9 1.425(16), C16–N7 1.431(16), N1–Pd1–N3 86.5(5), N1–Pd1–Cl2 177.8(4), N3–Pd1–Cl2 91.6(3), N1–Pd1–Cl1 91.9(4), N3–Pd1–Cl1 177.5(4), Cl2–Pd1–Cl1 89.99(18), N8–Pd2–N6 86.9(5), N8–Pd2–Cl3 177.0(4), N6–Pd2–Cl3 91.9(4), N8–Pd2–Cl4 91.3(3), N6–Pd2–Cl4 174.4(4), Cl3–Pd2–Cl4 89.72(16), C12–C11–N2 124.0(13), C12–C11–N4 119.9(13), N2–C11–N4 116.0(11), C11–C12–N5 126.0(13), C11–C12–C13 128.1(14), C16–C15–C14 128.5(13), N5–C15–C14 105.6(12), C15–C16–N9 122.2(13), C15–C16–N7 125.1(13), N9–C16–N7 112.8(12).

The X-ray structure of **9** is given in Fig. 7 along with the selected bond lengths and angles; its refinement data are given in Table 1. Complex **9** crystallizes in the monoclinic $P2_1/n$ space group and the asymmetric unit contains one molecule of **9**, one acetonitrile, and one and half molecules of water as the solvents of crystallization, formulated as **9**·CH_3CN·$1.5H_2O$. The X-ray structure revealed that the pyrazolyl nitrogen atoms on both sides of the molecule are chelated to the palladium metal atom, thus forming two six-membered palladacycles adopting a boat conformation. This type of boat conformation has been reported for several other palladium complexes containing pyrazolyl groups.[20] The molecule can also be regarded as a compartmental complex in which the two distorted square planar palladium(II) atoms are located above the plane formed by the pyrrole ring, methylene carbons and the pyrazolyl nitrogen atoms and are facing to each other, which can be regarded as *cis* orientation. This is in contrast to the structure of palladium(II) complex of 2,3,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)pyrrole in which the two palladium atoms are located above and below the pyrrole ring plane.[21] As compared to the free molecule **6**, upon coordination a significant decrease in the bond distance is observed for the pyrrole ring β C–C distance: C13–C14 = 1.317(19) Å in **9** against 1.363(10) Å in **6**. Further, the Pd–N(pz) and Pd–Cl bond distances fall within the range reported for the pyrazole nitrogen coordinated palladium complexes.[22] The molecule appears to be rigid as shown by the ^1H NMR spectrum displaying one separate singlet for each pyrazolyl CH proton and methyl group, probably because of the conjugation to be maintained. The pyrrolic NH group is hydrogen bonded to one of the co-crystallized water molecules and gives a broad singlet at 8.52 ppm in the ^1H NMR spectrum.

Conclusions

In conclusion, a new class of fluorescent quinoidal form of pyrrole with four high electron affinity nitrogen atoms attached to the methylene carbons causing it to act as an electron acceptor was developed through the dehydrogenation reaction of **1** with DDQ and represents the first structurally characterised molecule of its type. The cleavage of O_2 under sunlight demonstrates its quite reactive nature and gives insights about the possible biradical resonance structure. The isolated DDQ oxidation products are correlated with the isolated products of the reaction of the quinoidal pyrrole with oxygen. The structures for most of the compounds including binuclear palladium(II) complex are unambiguously established by X-ray diffraction method. Further reactions for adduct and metal complex synthesis are under progress.

Experimental Section

Experimental Section, General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. Work-up procedures including $NaHCO_3$ treatment were carried out under aerobic conditions. Petroleum ether (bp 40–60 °C) and other solvents were distilled according to the standard procedures. Other chemicals were obtained from commercial sources and used without further purification. ^1H NMR (200 MHz and 400 MHz) and ^{13}C NMR (50.3 MHz and 100.6 MHz) spectra were recorded on a Bruker ACF200 spectrometer. Chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. FTIR spectra were recorded using Perkin Elmer Spectrum Rx. High Resolution Mass Spectra (ESI) were recorded using the Xevo G2 Tof mass spectrometer (Waters). Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyzer. Melting points were determined in open capillaries and are corrected using benzophenone as a reference. UV-vis spectra were recorded using Varian Cary 5000 UV-vis-NIR spectrophotometer.

Synthesis of 2,5-bis(3,5-dimethylpyrazolylcarbonyl)pyrrole 2, and 5-{bis(3,5-dimethylpyrazolyl)methyl}pyrrole-2-carbaldehyde, 3

To a dichloromethane (~50 mL) solution of **1** (1.0 g, 3.13 mmol) at 0 °C was added solid DDQ (2.13 g, 9.4 mmol). The colour of the solution immediately changed to dark green. After stirring at room temperature for 2 h, a saturated aqueous $NaHCO_3$ solution (2 × 50 mL) was added to the solution and stirred under aerobic conditions. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed from the organic layer and the residue was loaded onto a silica gel column. Elution using ethyl acetate/petroleum ether (1:3, v/v) afforded the first fraction from which the solvent was removed to give **2** as a colourless solid (0.11 g, 0.35 mmol, 11%). Further elution using the same solvent gave the second fraction from which the solvent was removed under vacuum to give compound **3** as a colourless solid (0.19 g, 0.64 mmol, 20%). Single crystals of **2** were obtained by the slow evaporation of a solution of **2** in methanol. **3** was crystallized by layering petroleum ether upon a solution of **3** in CH_2Cl_2.

For **2**: mp 134 °C. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 13.00$ (br s, 1H, NH), 7.38 (d, 2H, pyrrole CH), 6.06 (s, 2H, pyrazole CH), 2.65 (s, 6H, CH_3), 2.38 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 51.3 MHz, 25 °C): $\delta = 157.7$, 152.9, 146.1, 129.2, 120.2, 111.0, 15.0, 14.3. FT-IR (KBr, cm^{-1}): $\nu = 3437$ (br, s), 3310 (s), 3112 (w), 2976 (w), 2923 (w), 1676 (vs), 1585 (m), 1518 (m), 1486 (m), 1411 (m), 1365 (s), 1340 (s), 1312 (m), 1275 (m), 1195 (m), 1148 (w), 1106 (m), 1028 (m), 968 (w), 870 (m), 816 (m), 768 (m), 731 (w), 627 (w). HRMS (+ESI): calcd *m*/*z* for [M + H$^+$] $C_{16}H_{18}N_5O_2$: 312.1455, found: 312.1458.

For **3**: mp 146 °C. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 10.74 (br s, 1H, NH), 9.54 (s, 1H, CHO), 7.60(s, 1H, CH), 6.93 (s, 1H, pyrrole CH), 6.25 (s, 1H, pyrrole CH), 5.80 (s, 2H, pyrazole CH), 2.22 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 51.3 MHz, 25 °C): δ = 179.5, 149.2, 141.1, 134.2, 132.7, 121.1, 111.5, 107.5, 67.9, 13.8, 11.5. IR (KBr, cm^{-1}): ν = 3299 (s), 2923 (w), 2865 (w), 1666 (s), 1555 (m), 1468 (m), 1418 (s), 1380 (m), 1316 (m), 1268 (w), 1223 (m), 1168 (s), 1116 (w), 1035 (m), 976 (w), 875 (w), 786 (s), 757 (m), 719 (m), 650 (w), 516 (w). HRMS (+ESI): calcd *m*/*z* for [M + Na]$^+$ $C_{16}H_{19}N_5ONa$: 320.1482, found: 320.1485.

Synthesis of 2-tri(3,5-dimethylpyrazolylmethyl)-5-(3,5-dimethylpyrazolylcarbonyl)pyrrole 4 and the DDQH$_2$ adduct of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole, 5

To a dichloromethane (~50mL) solution of **1** (1.0 g, 3.13 mmol) at 0 °C was added solid DDQ (2.13 g, 9.40 mmol). The colour of the solution immediately changed to dark green and stirring was continued for additional 2 h at room temperature. The solution was concentrated and loaded onto a silica gel column. Elution using ethyl acetate/petroleum ether (1:3, v/v) afforded the first fraction from which the solvent was removed to give **2** as a colourless solid (0.11 g, 0.35 mmol, 11%). Removal of the solvent from the second orange coloured fraction gave compound **5** as a yellow solid (0.5 g, 0.72 mmol, 22%). Slow evaporation of the reaction mixture in acetonitrile gave a few single crystals of **4**. Suitable single crystals of **5** were obtained by the slow evaporation of a solution of **5** in toluene at room temperature.

For **4**: ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 12.04 (br s, 1H, NH), 5.99 (s, 1H, pyrazole CH), 5.91 (s, 3H, pyrazole CH), 5.79 (dd, *J* = 4.0, 2.4 Hz, 2H, pyrrole CH), 2.62 (s, 3H,

CH_3), 2.27 (s, 3H, CH_3), 2.17 (s, 9H, CH_3), 1.69 (s, 9H, CH_3). Further characterization could not be carried out because of its very low yield.

For **5**: mp 140 °C (decomposed). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 9.64 (br s, 1H, NH), 6.00 (s, 2H, pyrrole CH), 5.88 (s, 2H, pyrazole CH), 5.79 (s, 2H, pyrazole CH), 2.44 (s, 6H, CH_3), 2.34 (s, 6H, CH_3), 1.91 (s, 6H, CH_3), 1.75 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 51.3 MHz, 25 °C): δ = 151.8, 149.8, 149.7, 144.0, 141.0, 137.5, 133.4, 126.0, 113.6, 109.0, 107.6, 106.8, 106.2, 14.0, 13.5, 11.0, 10.6. IR (KBr, cm^{-1}): ν = 3222 (br, s), 2925 (w), 2526 (w), 2364 (w), 2251 (m), 1661 (w), 1564 (m), 1450 (s), 1414 (m), 1355 (s), 1274 (m), 1193 (s), 1078 (w), 1039 (w), 979 (w), 891 (m), 778 (w), 692 (w), 623 (w). HRMS (+ESI): calcd *m*/*z* for $[M + Na]^+$ $C_{34}H_{33}Cl_2N_{11}NaO_2$: 720.2093, found: 720.2114. UV-vis (DMSO): λ_{max}, nm (ε, $M^{-1}cm^{-1}$) = 421 (35000), 442 (32200) and 326 (11200).

Synthesis of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole 6 from 5

Method A: To a solution of **5** (1.0 g, 1.43 mmol) in dry MeOH (~50 mL) at 0 °C was added solid $NaBH_4$ (2.7 g, 71.50 mmol) slowly. The solution was stirred at room temperature for 16 h. After adding water (~150 mL) to the solution, the solution was extracted with dichloromethane (50 mL) three times. The dichloromethane solution was dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated and loaded onto a silica gel column. Elution using ethyl acetate/petroleum ether (1:2, v/v) gave the first fraction from which the solvent was removed to give **6** as yellow solid (0.45 g, 0.96 mmol, 67%). mp 147 °C. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 9.42 (br s, 1H, NH), 6.22 (d, 2H, pyrrole CH), 5.90 (s, 2H, pyrazole CH), 5.82 (s, 2H, pyrazole CH), 2.28 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 1.69 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 51.3 MHz, 25 °C): δ = 149.7, 149.4, 143.2, 140.9, 137.8, 126.7, 109.5, 107.2, 106.4, 14.0, 13.8, 11.2, 10.5. IR (KBr, cm^{-1}): ν = 3357 (m), 2956 (w), 2925 (w), 2861 (w), 1676 (w), 1647 (w), 1562 (m), 1454 (m), 1415 (s), 1358 (s), 1204 (w), 1117 (w), 1027 (w), 974 (w), 909 (w), 838 (w), 792 (m), 724 (w), 656 (w), 629 (w), 581 (w). HRMS (+ESI): calcd *m/z* for $[M + H]^+$ $C_{26}H_{32}N_9$: 470.2775, found: 470.2797. UV-vis (DMSO): λ_{max}, nm (ε, $M^{-1}cm^{-1}$) = 420 (23700), 443 (21900) and 259(16500).

Method B: A solution of **5** in ethyl acetate/petroleum ether (1/1, v/v) was passed through a basic alumina column. The first fraction was collected and the solvent was removed under vacuum to give an oily residue which was washed with hexanes to give **6** as yellow coloured solid. The ^{1}H and ^{13}C NMR spectra of **6** obtained by this way is identical to the one obtained from the above procedure, method A.

The Sunlight irradiation of 6

A solution of **6** (0.10 g, 0.21 mmol) in toluene (20 mL) was connected to a bladder containing oxygen gas and stirred under sunlight irradiation for 6 h at room temperature. The solvent was removed under vacuum and the residue was loaded onto a silica gel column. Elution using ethyl acetate/petroleum ether (1:5 v/v) gave the first fraction. Elution using ethyl acetate/petroleum ether (1:1 v/v) gave the second and the third fractions. Removal of solvents from these fractions under vacuum gave compound **2** as colourless solid (0.01 g, 0.032 mmol, 15%), compound **7** as a colourless oil (0.008 g, 0.037 mmol, 17%) and compound **8** as a colourless solid (0.03 g, 0.11 mmol, 50%), respectively. The identity of **2** obtained from this method was confirmed after comparing the NMR and IR data with those of **2** obtained from the reaction of **1** with DDQ described above.

For bis-(3,5-dimethylpyrazolyl)methanone[23] **7**: ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 5.85$ (s, 2H, pyrazole CH), 2.28 (s, 12H, CH_3). IR (KBr, cm^{-1}): $\nu = 3440$ (s), 2925 (m), 2852 (m), 1740 (m), 1699 (s), 1650 (s), 1560 (m), 1541 (m), 1513 (w), 1460 (m), 1418 (w), 1393 (w), 1261 (w), 1189 (w), 1105 (s), 1029 (w), 800 (w), 697 (w), 629 (w). HRMS (+ESI): calcd *m*/*z* for $[M + H]^+$ $C_{11}H_{15}N_4O$: 219.1246, found: 219.1292.

For 2-(3,5-dimethylpyrazolylcarbonyl)-5-(3,5-dimethylpyrazolyl)pyrrole **8**: ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 8.85 (br s, 1H, NH), 6.84 (dd, *J* = 5.6, 1.6 Hz, 1H, pyrrole CH), 6.13 (dd, *J* = 5.6, 1.6 Hz, 1H, pyrrole CH), 5.99 (s, 1H, pyrazole CH), 5.90 (s, 1H, pyrazole CH), 2.27 (s, 3H, CH_3), 2.26 (s, 3H, CH_3) 1.97 (s, 3H, CH_3), 1.60 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 51.3 MHz, 25 °C): δ = 171.3, 152.4, 151.1, 143.6, 142.4, 136.3, 129.4, 124.8, 116.8, 109.3, 107.9, 13.9, 13.7, 11.0, 10.3. IR (KBr, cm^{-1}): ν = 3384(m), 3250(m), 2925(s), 2856(m), 1700(vs), 1567(s), 1450(s), 1393(s), 1352(s), 1235(w), 1192(m), 1119(m), 1073(m), 1033(m), 975(m), 915(m), 807(s), 732(s), 799(m), 632(w), 590(w), 513(w). HRMS (+ESI): calcd *m*/*z* for $[M + H]^+$ $C_{15}H_{18}N_5O$: 284.1506, found: 284.1581.

Synthesis of $[Pd_2Cl_4\{\mu\text{-}C_4H_3N\text{-}2,5\text{-}(C(Me_2pz)_2)_2\text{-}N,N,N,N\}]$, 9

To a solution of $[Pd(PhCN)_2Cl_2]$ (0.045 g, 0.12 mmol) in toluene (10 mL) was added **6** (0.028 g, 0.059 mmol). The solution was stirred at room temperature for 16 h to give a brown precipitation of **9**. The solution was filtered and the precipitate was washed with diethyl ether (3×10 mL) and then dried under vacuum. Yield: 72% (0.035 g, 0.042 mmol). Suitable single crystal of **9** was grown from an acetonitrile solution of **9** by the slow evaporation. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 8.52 (br s, 1H, NH), 6.90 (s, 2H, pyrrole CH), 6.03 (s, 2H, pyrazole CH), 5.98 (s, 2H, pyrazole CH), 2.58 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 2.38 (s, 6H, CH_3). IR (KBr, cm^{-1}): ν = 3454 (br), 3126 (w), 2961 (w), 2930 (w), 1656 (m), 1625 (m), 1561 (m), 1464 (m), 1416 (m), 1393 (m), 1261 (m), 1098 (s), 803 (m), 654 (w), 471 (w). HRMS (+ESI): calcd *m*/*z* for $[M - 2Cl + Na]^+$ $C_{26}H_{31}Cl_2N_9NaPd_2$: 774.0041, found: 774.0657. UV-vis (acetonitrile): $\lambda_{max}(\varepsilon)$ = 371 nm (32400 $M^{-1}cm^{-1}$).

X-ray Crystallography

Suitable single crystals of **2−6** and **9** were obtained from solvents mentioned in their respective synthetic procedures. Single crystal X-ray diffraction data collections for these crystals were performed using a Bruker-APEX-II CCD diffractometer with graphite monochromated molybdenum Kα radiation (λ = 0.71073 Å). The structures were solved by SIR-92[24] available in the WinGX program which successfully located most of the non-hydrogen atoms. Subsequently, least-squares refinements were carried out on F2 using SHELXL-97[25] (WinGX version) to locate the remaining non-hydrogen atoms. Typically for all the structures, hydrogen atoms attached to carbon atoms were fixed in calculated positions. The pyrrolic NH or OH hydrogen atoms were located from the difference Fourier map and freely refined isotropically with their thermal parameters set as equivalent to 1.2 times that of their parent atoms. In the case of structure of **9**, water hydrogens are not appearing and hence not located; and the pyrrolic NH hydrogens are fixed. Crystallographic refinement data are given in Table 1.

Table 1. Crystallographic data for compounds **2-6** and **9**.

	2	**3**	**4**	**5**	**6**	**9**
Empirical formula	$C_{16}H_{17}N_5O_2$	$C_{16}H_{19}N_5O$	$C_{26}H_{31}N_9O$	$C_{34}H_{33}Cl_2N_{11}O_2$	$C_{26}H_{31}N_9$	$C_{28}H_{37}Cl_4N_{10}O_{1.5}Pd_2$
Formula weight	311.35	297.36	485.60	698.61	469.60	892.28
Wavelength (Å)	0.71073	1.54178	0.71073	0.71073	0.71073	0.71073
Temperature (K)	293(2)	110(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	*Cc*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$Pna2_1$	$P2_1/n$
a/Å	19.167(6)	8.6780(9)	19.389(3)	8.1453(7)	23.991(4)	13.058(3)
b/Å	4.5557(15)	10.1309(12)	13.8717(17)	12.1246(10)	8.3841(13)	15.125(3)
c/Å	18.226(6)	10.3932(11)	9.8796(12)	18.4077(16)	25.825(4)	20.479(4)
α/degree	90.00	104.171(6)	90.00	106.647(3)	90.00	90.00
β/degree	100.720(10)	108.391(6)	104.655(4)	99.820(3)	90.00	106.625(7)
γ/degree	90.00	110.259(6)	90.00	94.826(3)	90.00	90.00
Volume(Å^3)	1563.7(9)	746.32(14)	2570.7(6)	1699.1(3)	5194.6(13)	3875.6(13)
Z	4	2	4	2	8	4
D_{calcd} , g cm^{-3}	1.322	1.323	1.255	1.366	1.201	1.529
μ/mm^{-1}	0.091	0.702	0.082	0.241	0.076	1.241
F(000)	656	316	1032	728	2000	1788
θ range(degree)	2.16 to 25.38	4.89 to 59.08	1.09 to 25.34	1.18 to 25.00	1.58 to 25.00	1.66 to 25.00
Limiting indices	– 22<=h<=22, – 5<=k<=5, –21<=l<=21	– 9<=h<=9, – 11<=k<=10, –11<=l<=11	– 23<=h<=23, – 16<=k<=16, – 10<=l<=11	– 9<=h<=9, – 14<=k<=14, – 21<=l<=21	–28<=h<=28, –9<=k<=9, –29<=l<=30	– 14<=h<=15, – 17<=k<=17, – 24<=l<=24
Total/ unique no. of reflns.	8729/2449	8494/2031	30038/4528	20611/5978	59470 / 8778	44801 / 6824

R_{int}	0.0404	0.0985	0.1460	0.0825	0.2162	0.2343
Data / restr./params.	2449 / 2 / 212	2031 / 0 / 207	4528/ 0 / 328	5978/0/451	8778 / 1 / 638	6824 / 0 / 415
GOF(F^2)	1.007	0.942	1.005	1.002	1.106	1.002
$R1$, $wR2$	0.0553, 0.1353	0.0362, 0.0886	0.0726, 0.1659	0.0625, 0.1393	0.0945, 0.1616	0.0924, 0.2214
$R1$, $wR2$ (all data)	0.0829, 0.1532	0.0428, 0.0909	0.1961, 0.2341	0.1418, 0.1806	0.2114, 0.2085	0.2083, 0.2836
peak and hole (e Å^{-3})	0.197 and −0.170	0.159 and −0.236	0.296 and −0.283	0.346 and −0.329	0.200 and −0.281	1.685 and − 0.603

Acknowledgements

We thank the CSIR and DST for support and for the X-ray and NMR facilities. We also thank Dr. Joseph H. Reibenspies, Department of Chemistry, Texas A&M University for one data collection and structure refinement.

Notes and references

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1 (*a*) D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153; (*b*) L. Yu, K. Muthukumaran, I. V. Sazanovich, C. Kirmaier, E. Hindin, J. R. Diers, P. D. Boyle, D. F. Bocian, D. Holten and J. S. Lindsey, *Inorg. Chem.*, 2003, **42**, 6629; (*c*) S. B. Bharate, *Synlett*, **2006**, 496.

2 (*a*) H. Liu, L. Cao, J. Sun, J. S. Fossey and W.-P. Deng, *Chem. Commun.*, 2012, **48**, 2674; (*b*) S. Bhunia, S. Ghosh, D. Dey and A. Bisai, *Org. Lett.*, 2013, **15**, 2426; (*c*) Z.-L. Wang, H.-L. Li, L.-S. Ge, X.-L. An, Z.-G. Zhang, X. Luo, J. S. Fossey and W.-P. Deng, *J. Org. Chem.*, 2014, **79**, 1156.

3 K. Ohkubo, A. Fujimoto and S. Fukuzumi, *J. Am. Chem. Soc.*, 2013, **135**, 5368.

4 (*a*) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 7190; (*b*) S. Ramakrishnan, K. S. Anju, A. P. Thomas, E. Suresh and A. Srinivasan, *Chem. Commun.*, 2010, **46**, 4746.

5 (*a*) J. L. Sessler, R. S. Zimmerman, C. Bucher, V. Král and B. Andrioletti, *Pure Appl. Chem.*, 2001, **73**, 1041; (*b*) T. E. Wood and A. Thompson, *Chem. Rev.*, 2007, **107**, 1831; (*c*) T. Guchhait, V. K. Jha and G. Mani, *Org. Biomol. Chem.*, 2013, **11**, 2818.

6 J.-Y. Shin, S. S. Hepperle, B. O. Patrick and D. Dolphin, *Chem. Commun.*, 2009, 2323.

7 J.-Y. Shin, B. O. Patrick and D. Dolphin, *Org. Biomol. Chem.*, 2009, **7**, 2032.

8 J.-Y. Shinab and D. Dolphin, *New J. Chem.*, 2011, **35**, 2483.

9 D. Ghorai, S. Kumar and G. Mani, *Dalton Trans.*, 2012, **41**, 9503.

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10 I. Rozas, I. Alkorta and J. Elguero, *J. Phys. Chem. A*, 1998, **102**, 9925.

11 I. A. Guzei, L. C. Spencer, M. G. Tshivashe and J. Darkwa, *Acta Cryst.*, 2009, **E65**, o2743.

12 E. J. Poziomek, R. A. Mackay, and T. J. Novak, *Mikrochim. Acta* 1974, **62**, 281.

13 (*a*) E. Gebert, Jr. A. H. Reis, J. S. Miller, H. Rommelmann and A. J. Epstein, *J. Am. Chem. Soc.*, 1982, **104**, 4403; (*b*) A. O. Patil, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 1984, **106**, 4010; (*c*) M. Bouvet, B. Malezieux and P. Herson, *Chem. Commun.*, 2006, 1751; (*d*) C. Yi, S.-X. Liu, A. Neels, P. Renaud and S. Decurtins, *Org. Lett.*, 2009, **11**, 5530; (*e*) X. Guegano, J. Hauser, S.-X. Liu and S. Decurtins, *Acta Cryst.*, 2011, **E67**, o2967.

14 Y. Qiao, J. Zhang, W. Xu, D. Zhu, *J. Mater. Chem.* 2012, **22**, 5706.

15 (a) T. M. Pappenfus, B. J. Hermanson, T. J. Helland, G. G. W. Lee, S. M. Drew, K. R. Mann, K. A. McGee, and S. C. Rasmussen, *Org. Lett.* 2008, **10**, 1553; (b) Y. A. Getmanenko, T. A. Purcell, D. K. Hwang, B. Kippelen, and S. R. Marder, *J. Org. Chem.*, 2012, **77**, 10931.

16 (*a*) S. Gronowitz and B. Uppstrom, *Acta Chem. Scand. B*, 1974, **28**, 981; (*b*) A. Ishii, Y. Horikawa, I. Takaki, J. Shibata, J. Nakayama and M. Hoshino, *Tetrahedron Lett.*, 1991, **32**, 4313.

17 (*a*) K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami and Y. Fukazawat. *J. Am. Chem. Soc.*, 1991, **113,** 4576. (*b*) T. Takahashi, K.-I. Matsuoka, K. Takimiya, T. Otsubo and Y. Aso, *J. Am. Chem. Soc.*, 2005, **127**, 8928; (*c*) S. D. Motta, F. Negri, D. Fazzi, C. Castiglioni and E. V. Canesi, *J. Phys. Chem. Lett.*, 2010, **1**, 3334; (*d*) E. V. Canesi, D. Fazzi, L. Colella, C. Bertarelli and C. Castiglioni, *J. Am. Chem. Soc.*, 2012, **134**, 19070; *(e)* J. Casado, R. P. Ortiz and J. T. L. Navarrete, *Chem. Soc. Rev.,* 2012, **41**, 5672; (*f*) T. M. Pappenfus, K. B. Schliep, A. Dissanayake, T. Ludden, B. Nieto-

---

Ortega, J. T. L. Navarrete, M. C. R. Delgado, and J. Casado, *J. Chem. Educ.* 2012, **89**, 1461.

18 L. K. Montgomery, J. C. Huffman, E. A. Jurczak and M. P. Grendze, *J. Am. Chem. Soc.*, 1986, **108,** 6004.

19 (*a*) A. Kikuchi, F. Iwahori and J. Abe, *J. Am. Chem. Soc.*, 2004, **126**, 6526; (*b*) M. Abe, *Chem. Rev.*, 2013, **113**, 7011.

20 (*a*) M. C. Carrion, G. Dura, F. A. Jalo, B. R. Manzano, and A. M. Rodríguez, *Cryst. Growth Des.,* 2012, **12**, 1952; (*b*) A. Sánchez-Méndez, E. de Jesús, J. C. Flores, and P. Gómez-Sal, *Eur. J. Inorg. Chem.,* 2010, 1881; (*c*) S. Tsuji, D. C. Swenson, and R. F. Jordan, *Organometallics,* 1999, **18**, 4758.

21 D. Ghorai, and G. Mani, *Inorg. Chem.*, **2014**, *53*, 4117.

22 (*a*) G. Minghetti, M. A. Cinellu, A. L. Bandini, G. Banditelli, F. Demartin, and M. Manassero, *J. Organomet. Chem.,* 1986, **315**, 387; (*b*) N. Arroyo, F. Gomez-de la Torre, F. A. Jalon, B. R. Manzano, B. Moreno-Lara, and A. M. Rodríguez, *J. Organomet. Chem.,* 2000, **603**, 174; (*c*) J. Garcia-Anton, J. Pons, X. Solans, M. Font-Bardia, and J. Ros, *Eur. J. Inorg. Chem.,* 2002, 3319; (*d*) M. P. Conley, C. T. Bruns, and R. F. Jordan, *Organometallics,* 2007, **26**, 6750; (*e*) A. Sánchez-Méndez, E. de Jesús, J. C. Flores, and P. Gómez-Sal, *Inorg. Chem.,* 2007, **46**, 4793; (*f*) A. John, M. M. Shaikh, R. J. Butcher, and P. Ghosh, *Dalton Trans.,* 2010, **39**, 7353; (*g*) A. Sánchez-Méndez, E. de Jesús, J. C. Flores, and P. Gómez-Sal, *Eur. J. Inorg. Chem.,* 2010, 141; (*h*) A. J. Hallett, C. J. Adams, K. M. Anderson, R. A. Baber, N. G. Connelly, and C. J. Prime, *Dalton Trans.,* 2010, **39**, 5899.

23 T. C. Higgs, and C. J. Carrano, *Inorg. Chem.* 1997, **6**, 291.

24 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.* **1993**, *26*, 343.

25 G. M. Sheldrick, "A short history of SHELX", *Acta Crystallogr.* **2008**, *A64*, 112.

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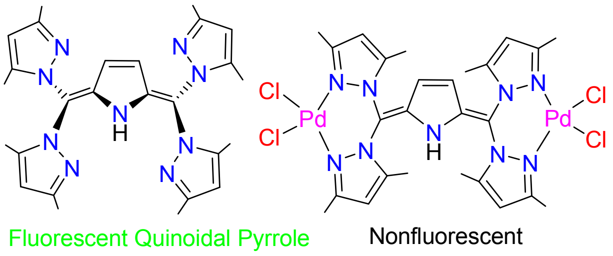

A new class of reactive quinoidal structure of pyrrole, which forms donor-acceptor and binuclear palladium complexes, and the products of its reaction with O_2 only under sunlight are described.

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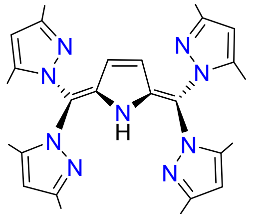

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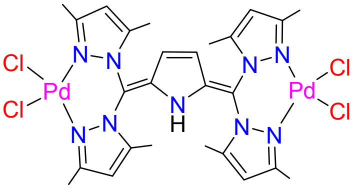

Nonfluorescent

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