Di- vs tetra-substituted quinonediimines: a drastic effect in coordination chemistry

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We describe the first isolation of N,N'-disubstituted benzoquinonediimines (QDIs) **2** which revealed drastically different properties compared to N,N',N'',N'''-tetrasubstituted QDIs **1** because of the absence of N-substituents in the "upper part" of the molecule. Three major differences could be highlighted thanks to the present joint experimental and theoretical investigation : 1) their metalation with different metal precursors revealed a specific behaviour in coordination chemistry giving access to novel complexes with unprecedented stoichiometry and remarkable absorption properties. More specifically, a new monoplatinum complex, able to absorb light from the UV up to the NIR region because of its unique delocalization pathway across the metal centre, was obtained; 2) this new class of di-substituted QDIs showed an exceptionally broad pK_a range ($\Delta pK_a \sim 8$) that could be explained by the possible tuning of the basicity of each imine which is now attainable; 3) these quinones could be used as reagent in organic synthesis to form N,N',N'',N'''-tetrasubstituted QDIs with tuneable substituents (aryl vs alkyl), previously unknown, as new ligand for coordination chemistry.

Introduction

Quinoidal molecules have attracted extraordinary attention for decades because of their remarkable fundamental features and their diverse applications in many fields ranging from organic and coordination chemistry to biology and physics.¹⁻⁴ Among them, 2,5-diamino-1,4-benzoquinonediimines (QDIs) **1** are particularly interesting because of the unusual distribution of their overall 12- π electrons system which can be described as two nearly-independent 6- π electrons subunits chemically connected through two C-C single bonds. This unique distribution (*i.e.*, the so-called "coupling principle") – first suggested 50 years ago based on theoretical studies of 12- π electrons quinones,⁵ was confirmed experimentally in 2003, giving rise to fascinating optical properties.⁶ Aside, QDIs of type **1** appeared also to be reagents of choice in organic chemistry as precursors of benzobisimidazole derivatives,⁷ or in analytical chemistry as efficient proton sensors in the intracellular pH range.^{6,8} Importantly, their coordination chemistry has been the subject of numerous investigations during the last two decades, and these studies clearly demonstrated the very rich and versatile behaviour of QDIs **1** as ligand for the preparation of mono and dinuclear complexes (M = Ru, Fe, Cu, Pd, Ni, Zn, Ir, W, Re, Na, Li, B) exhibiting valuable properties in several technological sectors.⁹⁻¹⁸ We also highlighted that the unsubstituted parent **3** behaves differently from **1** in coordination chemistry owing to the absence of N-substituents that allows the formation of polynuclear complexes with controlled lengths.¹⁹ These observations suggest the study of QDIs **2** that can be viewed as the hybrid form of **1** and **3**.

N,N'-disubstituted QDIs **2** are hitherto unknown probably owing to the high reactivity of the unsubstituted imines that easily undergo side-reactions such as hydrolysis.²⁰ Nevertheless, the substitution pattern in **2** is of peculiar interest because the absence of N-substituents in the "upper part" of this compound should prevent steric hindrance and allow a modulation of the electronic density on the nitrogen atoms, inducing drastically different properties compared to **1**.

Therefore, performing the synthesis of **2** appeared as a very attractive target to pave the way to new properties based on a specific coordination chemistry. Herein, we report an efficient preparation of N,N'-disubstituted QDIs **2** and demonstrate the higher versatility of these new unhindered but yet soluble ligands in coordination chemistry, compared with their N,N',N'',N'''-tetrasubstituted analogues **1**. The use of **2** as reagent in organic synthesis was also investigated due to a specific reactivity of the unsubstituted amino-enamine moiety²¹ that allowed the access to N,N',N'',N'''-tetrasubstituted QDI ligand **4** bearing simultaneously aryl and alkyl substituents, previously unknown. Spectrophotometric and theoretical studies were additionally

performed to evaluate the impact of the absence/presence of N-substituents on the acido-basic properties of **2**, and to obtain first insights into the structure-property relationships of these new complexes.

Results and discussion

Synthesis. The commercially available 1,5-fluoro-2,4-dinitrobenzene **5** was first reacted with primary amines R-NH₂ **6a-d** in EtOH or MeCN in the presence of base to afford **7a-d** as yellow or orange powder in high yields (Scheme 1). The electron-poor aryl **5** was identified as a coupling partner of choice owing to, on the one hand, the presence of structural elements for nucleophilic aromatic substitutions (S_NAr) and, on the other hand, the possibility to obtain N-substituted 1,3-diaminobenzenes of type **7** functionalised by nitro groups.

Scheme 1 Synthesis of QDI **2a-e**. **8e** was prepared as described in the literature.²²

Their ¹H NMR spectra show the NH resonances in the range 9.2–9.7 ppm consistent with the presence of intramolecular hydrogen bonds with the NO₂ functions.

Next, the two NO₂ groups in **7a-d** were reduced by SnCl₂ in acidic medium affording the corresponding tetraamino-benzene derivatives **8a-d**·2HCl that could be isolated as beige solids in their diprotonated form. In presence of base (K₂CO₃), the electron-rich molecules **8a-e** are then able to sacrifice - by air oxidation - their aromatic character in favour of QDIs **2a-e** that could be isolated in good yields (under neutral form), and fully characterized including by X-ray diffraction for **2a** (Fig. 1). The ¹H NMR spectrum of **2a** revealed the presence of two resonances at 5.95 and 5.71 ppm consistent with non-aromatic C-H protons. DFT calculations of the NICS(0) at the centre of the cycle indeed found a positive value (+4.23 ppm) also consistent with an anti-aromatic character. The single crystal X-ray analysis confirmed the presence of two aryl groups and established its *p*-benzoquinonediimine form (Fig. 1). Examination of the bond distances within the N(3)-C(3)-C(4)-C(5)-N(4) and N(2)-C(2)-C(1)-C(6)-N(1) moieties reveals a localised π-system, whereas the C(2)-C(3) and C(6)-C(5) distances of 1.490(2) and 1.497(2), respectively, indicate a dominating single-bond characters. All these values are in agreement with the presence of two nearly-independent 6-π subunits chemically connected by two C-C single bond as already observed for this class of 12-π electrons quinones.^{6,7}

Fig. 1 X-ray structure of **2a**. Selected bond lengths (Å): N(3)-C(3) = 1.350(2), C(3)-C(4) = 1.350(2), C(5)-N(4) = 1.280(2), N(2)-C(2) = 1.287(2), C(2)-C(1) = 1.433(2), C(1)-C(6) = 1.353(2), C(6)-N(1) = 1.364(2), C(3)-C(2) = 1.490(2), C(5)-C(6) = 1.497(2).

Molecule **2a** was also investigated as precursor in organic synthesis because of the presence of the unsubstituted amino-enamine subunit that should allow a transamination reaction in acidic medium by analogy with **3** (Scheme 2).²¹ As expected, the condensation between **2a** and alkyl primary amines such as octylamine in presence of HCl afforded in MeOH the corresponding tetra-substituted compound **4a** as a red oil in 72% yield. The reaction occurred through the monoprotonated species **A**, generated *in situ*, for which the positive charge is shared though H-transfer between the “lower” (tautomer **A**) and “upper” (tautomer **B**) parts of the molecule, leading to two degenerated tautomers in equilibrium in solution, *i.e.*, the average structure **C**. The transamination reaction itself occurs on the unsubstituted cyanine-type moiety (“upper” part) which is much more electrophile than the substituted one (“lower” part). The synthesis of **4a** could be also achieved from **8a** in a one-pot reaction in which **2a** was formed *in situ* and directly reacted with the octylamine (Scheme 2). The isolation of **4a** stands as the first example of QDI ligand bearing simultaneously aryl and alkyl N-substituents, demonstrating that one can fine-tune the electron density on the nitrogen atoms.

Scheme 2 Synthesis of mixed QDI **4a**

UV-Vis Absorption Spectroscopy. We then selected **2a** to undertake an absorption spectrophotometric study coupled to potentiometry in order to highlight the impact of the absence/presence of N-substituents on the acido-basic properties by comparison with acidochromic dyes based on **1** (see the ESI† for details).⁸ Due to the limited aqueous solubility of **2a**, the

physico-chemical investigations were performed in CH₃OH/H₂O (80/20 w/w). Two distinct pH ranges (very acidic and neutral) in which significant spectral variations on **2a** occurred were clearly evidenced. The absorption vs. pH titrations (see the ESI[†]) were statistically processed and allowed evaluating the pK_a values of **2a**, as well as the electronic absorption spectra of the protonated species (Fig. 2). Compound **2a** is characterized by two pK_a separated by about eight pK_a units (pK_{a1} = 0.2(2); pK_{a2} = 8.1(1)). The neutral form **2a** presents an intense absorption at 354 nm (mostly intra-ring transitions, $\epsilon^{354} = 1.28 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) together with absorption shoulders extending to the visible region and presenting significant charge transfer characters (see theoretical calculations in the ESI[†]). Stepwise protonations of **2a** are characterized by bathochromic shifts of its transitions with appearance of noticeable visible and NIR absorptions. Theoretical calculations reveal that the first protonation takes place mostly on the N(2) atom rather than on the N(4) atom (see the ESI[†]) and the computed electronic spectra agree well with their experimental counterparts for both the neutral and mono-protonated forms.

Fig. 2 Electronic absorption spectra of the protonated species of **2a**. Solvent: CH₃OH/H₂O; *I* = 0.1 M NBu₄ClO₄; *T* = 25.0(2) °C.

The first protonation constant pK_{a2} = 8.1(1) compares well to values reported for related *N*-alkylated QDIs **1** with R = benzyl (pK_a = 7.96(5)), R = neopentyl (pK_a = 8.28(5)) or phenyl (pK_a = 6.6).⁸ No comparison could be however made for the second protonation process due to the extremely scarce pK_a values available for unsubstituted QDI, *i.e.*, *p*-benzoquinone-monoimine or *p*-benzoquinone-diimine are rather unstable and undergo hydrolysis in aqueous solutions. The unexpected large difference between the two pK_a values for **2a** ($\Delta pK_a \approx 8$) can be rationalized by considering the pK_as measured for various benzoquinone-monoimines (pK_a $\approx$ 3.0-3.5) as a benchmark²³ for **2a**-H⁺ (see the ESI[†] for details). Indeed, the significant decrease to a pK_a value close to 0 can be explained as a consequence of the strong electrostatic repulsions between the two independent conjugated subunits in **2a**-2H⁺. This effect - already emphasized for **1** with R = benzyl ($\Delta pK_a = 2.2$) or neopentyl ($\Delta pK_a = 2.6$)⁸ - appeared to be much stronger for **2a** giving account for the remarkable influence of the number of N-substituents on the acido-basic properties of 12- π electrons QDIs. To the best of our knowledge, molecule **2a** is a unique example of a quinoidal acidochrom able to absorb photons up to the NIR region.

Coordination chemistry. We also investigated the metal coordination properties of the new ligand **2a** in order to evaluate if a different behaviour could be highlighted compared with tetra-substituted analogues **1**. We first considered its metalation with Ni(acac)₂ because this metal precursor was successfully reacted with **1** to afford dinuclear complexes **9a** with R = alkyl or aryl (Scheme 3).¹⁷ Under similar and/or modified conditions (M:L ratio, solvent, reaction time), we did not isolate the expected dinuclear species, but observed instead the formation of a mixture of oligomers of type **11** that could not be separated (Scheme 4).

Scheme 3 Metalation of ligands **1**

Analysis of the mixture by mass spectrometry confirmed the presence of extended oligomers (with a highest-mass cluster of peaks centred at 4981.357 a.m.u up consistent with a Ni₁₀ isotopic distribution) that can absorb light up to the near infra-red (NIR) region, as displayed by the intense absorption band centred at 842 nm (Fig. 3).

Scheme 4 Metalation of **2a** ($R = 3,4,5-(OMe)_3C_6H_2$) with $Ni(acac)_2$

This behaviour partly parallels the case of ligand **3**, which also underwent an oligomerization process that could be explained by the absence of N-substituents, but which on the other hand allowed the isolation of each oligomer because of their higher stability.¹⁹

Fig. 3 Absorption spectrum of the mixture of oligomers **11** in $CHCl_3$.

Then, we considered a less reactive metal precursor such as Pt(II) in order to control the oligomerization process. Previous works reported the absence of reaction when N-substituted QDI **1** ($R = \text{alkyl}$) was mixed with $Pt(acac)_2$ owing to the reduced reactivity of the Pt precursor.¹³ To overcome this issue, the use of $[PtCl_2(COD)]$ on **1** was envisaged and allowed the formation of a diplatinum complex **10** ($R = \text{neopentyl}$), highlighting the crucial role of the ancillary ligand on the reactivity of the Pt centre (see Scheme 3).¹⁴ This prompted us to study first the metalation of **2a** with $[PtCl_2(COD)]$. As expected, we observed the formation of **12** showing a similar reactivity between **2a** and **1** (Scheme 5). In contrast, if $Pt(acac)_2$ does not react with QDI ligands **1**, we have now found that its reaction with **2a** in a 2:1 ligand/metal ratio (in heptane at 150°C in a sealed tube) readily afforded a new square-planar neutral complex **13** as a deep violet solid (Scheme 3). Its ¹H NMR spectrum shows two singlets at 5.20 and 5.78 ppm corresponding to quinoidal C-H protons, and two resonances at 7.82 and 6.92 ppm characteristic of the NH ($I = 2$) and NH₂ ($I = 4$) protons, respectively. We underline that when the same (drastic) conditions were used with N-substituted QDIs **1** ($R = \text{alkyl}$) and $Pt(acac)_2$, the starting materials were recovered confirming the strong influence of the substitution pattern on the reactivity of the ligand.

Scheme 5 Synthesis of **12**, **13** and **14** (R = 3,4,5-(OMe)₃C₆H₂)

This unique 1:2 metal/ligand ratio in QDI chemistry prompted us to study the metalation of **13** for which the two external sites could be – in principle – able to react with a cationic metal precursor. When **13** was reacted with Pt(acac)₂ under similar conditions (150°C), the formation of a complex mixture of polynuclear Pt complexes was observed probably due to the higher reactivity / lability of the “acac” moiety - in presence of unsubstituted nitrogen atoms – that allowed the oligomerization going further. In contrast, the use of [PtCl₂(COD)] in presence of base afforded the expected trinuclear species **14** as a blue solid in 91% yield (Scheme 5). This latter is stable in both solid state and solution because of the presence of the “COD” ancillary ligands that are inert with respect to the oligomerization process. As expected, the electronic spectrum of the diplatinum complex **12** reveals an absorption presenting a mixed metal-to-ligand charge transfer (MLCT) and intra-ligand (IL) character, centred (*vide infra*) at $\lambda_{\text{max}} = 504$ nm, as already observed for its analogue **10**.¹⁴ Interestingly, upon metalation of a Pt center (**13**), the absorption spectrum exhibits broad bands whose absorption maxima are lying in the visible at 555 nm and, importantly, extend up to 1000 nm in the NIR region (Fig. 4). The electronic absorption spectrum of **14** shows an absorption peak at $\lambda = 670$ nm with a shoulder at 614 nm, and absorbs rather poorly in the NIR region unlike in **13**. The pronounced bathochromic shift of the absorption for **14** with respect to that of **12** results from an extension of the delocalization of the conjugated π -system, whereas the differences between **13** and **14** were rationalized by theoretical calculations (*vide infra*).

Fig. 4 Absorption spectra recorded in DMSO at rt for **12**, **13**, and **14**.

Finally, we also investigated the metallation of new ligand **4a** with Ni(acac)₂ in order to confirm the key role of the number of N-substituents in the coordination chemistry of the QDIs. As expected, we did not observe an oligomerization process but the formation in 62% yield of **15** bearing simultaneously alkyl and aryl substituents, an exceptional feature in complexes based on QDI ligands. (Scheme 6).

Scheme 6 Metalation of **4a** with Ni(acac)₂

With respect to **12** and **10** (R = Np), complex **15** reveals a red-shifted absorption at $\lambda_{\text{max}} = 534 \text{ nm}$ ($\Delta\lambda = 30 \text{ nm}$), accounting for a significant effect of the presence of two different type of N-substituents. This band implies a HOMO-1 to LUMO transition, the former being highly-delocalized in the molecule, whereas the latter is centered on the QDI (see the ESI[†])

Theoretical Calculations. In order to gain more insights into the relationship between the electronic spectrum and the π -electron delocalization in these compounds, theoretical calculations were performed on **2a**, **12**, **13**, **14** and **15** using Time-Dependent Density Functional Theory (see the ESI[†] for details). A good match between experimental and calculated spectra is generally found. For **2a**, the theory reveals that the two lowest lying excited-states involve a significant charge-transfer character from the side Ph(OMe)₃ groups to the QDI core. In **12**, theory predicts an excited-state at rather long wavelength (652 nm), but it remains experimentally unseen as it present a trifling oscillator strength. The assignment of the band at 504 nm (computed at 483 nm) to a mixed MLCT/IL character is justified by the frontier MO displayed in Figure S5 in the ESI[†]. In **13**, the NIR transition is ascribable to a HOMO-LUMO transition presenting a significant oscillator strength (computed value: 0.29), whereas the intense band at ca. 555 nm mainly implies a HOMO-2 to LUMO transition (oscillator strength: 1.04). These orbitals are displayed in Fig. 5.

Fig. 5 HOMO-2 (bottom), HOMO (centre) and LUMO (top) of **13** (contour threshold: 0.02 au)

Fig. 6 Density difference plots between the relevant excited state of **14**. Blue and red regions indicate regions of decrease and increase of electron density upon absorption, respectively. Hydrogen atoms omitted for clarity. Contour threshold: 0.0004 au.

Electrochemistry. The electrochemical properties of the new compounds **2a-e**, **4a**, and **12-15** and of the protonated salt of **2a** were studied by recording their cyclic voltammograms (CV) in dichloromethane solutions (containing 0.1 M of $[(n\text{Bu}_4\text{N})\text{PF}_6]$, see Figures 7 and S34-35 in the ESI[†]). The corresponding half-wave potential values are summarized Table 1 and afford new insights into the effects of the number and nature of the N-substituents of QDI derivatives. When the electron-donating aryl groups of **2a** or **2b** are replaced by strong electron-withdrawing ones as in **2c**, the reduction process is shifted by *ca.* 400 mV while the first oxidation is shifted out of the solvent electrochemical window. The steric hindrance induced by the peripheral N-substituents has an unexpected impact on the energy associated with the oxidation of QDI ligands. For example, the two supplementary octyl chains introduced on **2a** giving **4a** produce an anodic shift of 200 mV of the first oxidation potential. This unexpected trend results probably from a different ligand conformation stabilizing the QDI ligand **4a** toward oxidation as illustrated by the highest potential value reached by **2d** bearing two bulky but still electron-donating cyclohexyl substituents.

Table 1: Half-wave potential (V vs. SCE) of **2a-e**, **4a**, and **12-15** (recorded in CH_2Cl_2 solutions containing 0.1 M of $[(n\text{Bu}_4\text{N})\text{PF}_6]$ with a scan rate of 100 mV/s).

	reduction		oxidation				ΔE^a
	2 nd	1 st	1 st	2 nd	3 rd	4 th	
2a	-	-1.20	0.47	1.09	-	-	1.67
2a·H⁺	-	-0.28	0.98	-	-	-	1.26
2b	-	-1.34	0.68	0.89	1.26	-	2.02
2c	-	-0.85	-	-	-	-	-
2d	-	-	0.84	1.47	-	-	-
2e	-	-	0.51	1.56	-	-	-
4a	-	-	0.67	1.06	1.33	-	-
12	-1.15 ^b	-0.68 ^b	0.70	0.80	1.38	-	1.38
13	-	-0.99	0.38 ^b	0.75	0.83	1.25	1.37
14	-1.02 ^b	-0.65 ^b	0.64	1.18	-	-	1.29
15	-	-	0.47	1.24	-	-	-

a. $\Delta E = E_{1/2}(1^{\text{st}} \text{ ox}) - E_{1/2}(1^{\text{st}} \text{ red})$; b. Reversible electrochemical processes.

On the other hand, the decreasing electrochemical gap accompanying the protonation of **2a** is in accordance with the resulting red-shifted absorption UV-Visible spectrum. The extended electronic delocalization of the frontier orbitals of the complexes **12**, **13** and **14** produces a lower HOMO-LUMO electrochemical gap compared to the parent ligand **2a**. Interestingly, the first oxidation of the monometallic complex **13** (Figure 7) and the two successive reductions of the bimetallic ones **12** and **14** are reversible and illustrate the potential use of **13** as an electron donor and of **12** and **14** as electron acceptors. The two irreversible oxidations of **15** have half-wave potential values close to those measured for previously described analogous tetra-N-substituted bis-nickel complexes.²⁴

Fig. 7 Cyclic voltammograms of **13**: a) first oxidation (reversible) and reduction processes; b) complete voltammogram.

Experimental

8e was synthesized as described in the literature.²²

Synthesis of N^1,N^3 -bis(3,4,5-trimethoxyphenyl)-4,6-dinitro-benzene-1,3-diamine (7a**):** To a solution of 1,5-difluoro-2,4-dinitrobenzene (2.00 g, 9.8 mmol, 1 equiv.) in EtOH (240 mL), were added 3,4,5-trimethoxyaniline (3.68 g, 20.1 mmol, 2.05 equiv.) and *N,N*-diisopropylethylamine (3.8 mL, 21.6 mmol, 2.2 equiv.). The mixture was heated to reflux for 4 hrs. The resulting precipitate was filtered, washed with EtOH and dried under vacuum to afford **7a** as an orange solid (4.48 g, 8.45 mmol, 87% yield). $R_f = 0.43$ (Silica F60, Ethyl acetate/Cyclohexane 50/50); ^1H NMR (400 MHz, CDCl_3): $\delta = 9.70$ (br s, 2H, N-H), 9.33 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 6.38 (s, 4H, Ar-H), 3.82 (s, 6H, OCH_3), 3.72 ppm (s, 12H, OCH_3); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.0, 147.3, 137.1, 132.7, 129.4, 125.1, 102.9, 94.8, 61.0, 56.3$ ppm; MS (ESI-TOF): calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_4\text{O}_{10}^+$ ($[\text{M}+\text{H}]^+$) 531.2, found 531.3; Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_{10}$: C, 54.34; H, 4.94; N, 10.56; found: C, 54.37; H, 4.80; N, 10.50.

Synthesis of N^1,N^3 -bis(3,5-bis(4-tertbutylphenyl)-4,6-dinitro-benzene-1,3-diamine (7b**):** To a solution of 1,5-difluoro-2,4-dinitrobenzene (0.500 g, 2.44 mmol, 1 equiv.) in MeCN (20 mL), were added 4-tert-butylaniline (0.764 g, 5.12 mmol, 2.1 equiv.) and *N,N*-diisopropylethylamine (0.931 mL, 5.36 mmol, 2.2 equiv.). The mixture was heated to reflux for 4 hrs. The resulting solid was filtered, washed with EtOH and dried under vacuum to afford **7b** as an orange solid (0.85 g, 1.84 mmol, 75% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 9.75$ (brs, 2H, N-H), 9.34 (s, 1H, Ar-H), 7.36 (d, $^3J_{\text{HH}} = 8.8$, 4H, Ar-H), 7.10 (d, $^3J_{\text{HH}} = 8.8$, 4H, Ar-H), 6.61 (s, 1H, Ar-H), 1.29 ppm (s, 18H, CH_3); ^{13}C (100 MHz, CDCl_3): $\delta = 149.7, 146.8, 134.5, 129.4, 126.4, 125.3, 124.1, 94.9, 34.5, 31.3$ ppm; HRMS (ESI-TOF): calcd. for $\text{C}_{26}\text{H}_{31}\text{N}_4\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 463.2340, found 463.2339.

Synthesis of N^1,N^3 -bis(3,5-bis(trifluoromethyl)phenyl)-4,6-dinitrobenzene-1,3-diamine (7c**):** Into a pressure bomb were introduced 1,5-difluoro-2,4-dinitrobenzene (1.10 g, 5.4 mmol, 1 equiv.), 3,5-bis(trifluoromethyl)aniline (2 mL, 12.8 mmol, 2.4 equiv.) and *N,N*-diisopropylethylamine (5.5 mL, 31.6 mmol, 5.9 equiv.). The bomb was then closed with a Teflon® seal and heated to 145 °C for 90 min. After cooling to room temperature, the resulting solid was taken up with EtOH and the insoluble compound was filtered, washed with EtOH and dried under vacuum to afford **7c** as an orange powder (2.52 g, 3.8 mmol, 70% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 9.95$ (br s, 2H, N-H), 9.39 (s, 1H, Ar-H), 7.74 (s, 2H, Ar-H), 7.60 (s, 4H, Ar-H), 6.46 ppm (s, 1H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 146.3, 138.5, 133.7$ (q, $^2J_{\text{FC}} = 34.3$ Hz), 129.4, 126.1, 125.4-125.5 (m), 122.4 (q, $^1J_{\text{FC}} = 264.8$ Hz), 120.7-120.8 (m), 94.5 ppm; HRMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{14}\text{N}_5\text{O}_4\text{F}_{12}^+$ ($[\text{M}+\text{NH}_4]^+$) 640.0849, found 640.0850.

Synthesis of N^1,N^3 -dicyclohexyl-4,6-dinitrobenzene-1,3-diamine (7d**):** To a solution of 1,5-difluoro-2,4-dinitrobenzene (3.00 g, 14.7 mmol, 1 equiv.) in EtOH (150 mL) were added cyclohexylamine (3.53 mL, 30.9 mmol, 2.1 equiv.) and *N,N*-diisopropylethylamine (5.38 mL, 30.9 mmol, 2.1 equiv.). The solution was heated to reflux for 2 hrs. The mixture was cooled to room temperature and the resulting precipitate was filtered, washed with EtOH and dried in vacuum to afford **7d** as a yellow solid (5.09 g, 14 mmol, 96% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 9.24$ (s, 1H, Ar-H), 8.34 (br d, $^3J = 6.5$ Hz, 2H, N-H), 5.72 (s, 1H, Ar-H), 3.43 (m, 2H, N-CH), 2.05 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 1.69 (m, 2H, CH_2), 1.48-1.37 ppm (m, 8H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.4, 130.0, 124.0, 90.7, 51.6, 32.1, 25.5, 24.3$ ppm; MS (ESI-TOF): calcd. for $\text{C}_{18}\text{H}_{27}\text{N}_4\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 363.2, Found 363.2; Elemental analysis: calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_4\text{O}_4$ C 59.65, H 7.23, N 15.46; found C 59.89, H 7.32, N 15.30.

Synthesis of N^1,N^5 -bis(3,4,5-trimethoxyphenyl)benzene-1,2,4,5-tetraamine dihydrochloride (8a): To a mixture of **7a** (500 mg, 0.94 mmol, 1 equiv.) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.70 g, 7.53 mmol, 8 equiv.) in a pressure bomb, were added HCl (12N, 10 mL) and Et_2O (4 mL). The bomb was closed with a Teflon® seal and the mixture was stirred at room temperature for 3 days. The resulting solid in suspension was filtrated, washed with HCl (12N) and Et_2O , dried under vacuum to afford the desired product **8a** as a pale powder (458 mg, 0.85 mmol, 90% yield); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.87 (br s, 2H, N-H), 7.23 (brs, 1H, Ar-H), 7.09 (br s, 1H, Ar-H), 6.20 (s, 4H, Ar-H), 3.62 (s, 12H, OCH_3), 3.57 ppm (s, 6H, OCH_3); HRMS (MALDI-TOF): calcd. for $\text{C}_{24}\text{H}_{30}\text{N}_4\text{O}_6^+$ ($[\text{M}]^+$) 470.2160, found 470.2160.

Synthesis of N^1,N^5 -bis(4-tertbutylphenyl)benzene-1,2,4,5-tetraamine dihydrochloride (8b): To a mixture of **7b** (3.00 g, 6.48 mmol, 1 equiv.) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (12.0 g, 53 mmol, 8 equiv.) in a pressure bomb, were added HCl (12N, 30 mL) and Et_2O (4 mL). The bomb was closed with a Teflon® seal and the mixture was stirred at room temperature for 3 days. The resulting solid in suspension was filtered, washed with HCl (12N) and Et_2O before being dried under vacuum to afford **8b** as a pale powder (3.1 g, 6.48 mmol, 100% yield); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.17 (br s, 4H, N-H), 8.33 (br s, 2H, N-H), 7.45 (s, 1H, Ar-H), 7.29 (d, $^3J_{\text{HH}}$ = 8.6 Hz, 4H, Ar-H), 7.03 (s, 1H, Ar-H), 6.96 (d, $^3J_{\text{HH}}$ = 8.6 Hz, 4H, Ar-H), 1.22 ppm (s, 18H, CH_3); HRMS (MALDI-TOF): calcd. for $\text{C}_{26}\text{H}_{34}\text{N}_4^+$ ($[\text{M}]^+$) 402.2778, found 402.2775.

Synthesis of N^1,N^5 -bis(3,5-bis(trifluoromethyl)phenyl)-benzene-1,2,4,5-tetraamine dihydrochloride (8c): To a mixture of **7c** (500 mg, 0.8 mmol, 1 equiv.) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.44 g, 6.43 mmol, 8 equiv.) in a pressure bomb, were added HCl (12N, 10 mL) and dichloromethane (4 mL). The bomb was closed with a Teflon® seal. The mixture was stirred at room temperature for 3 days. The resulting solid in suspension was filtrated, washed with HCl (12N), Et_2O and dried under vacuum to afford **8c** as a pale powder (458 mg, 0.72 mmol, 90% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 8.35 (br s, 2H, N-H), 7.22 (s, 1H, Ar-H), 7.07 (s, 5H, Ar-H), 7.07 ppm (s, 1H, Ar-H); HRMS (MALDI-TOF): calcd. for $\text{C}_{22}\text{H}_{15}\text{N}_4\text{F}_{12}^+$ ($[\text{M}+\text{H}]^+$) 563.1100, found 563.1103.

Synthesis of N^1,N^5 -dicyclohexylbenzene-1,2,4,5-tetraamine dihydrochloride (8d): To a mixture of **7d** (790 mg, 2.18 mmol, 1 equiv.) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3.94 g, 8 equiv.) in a pressure bomb, were added HCl (12N, 7 mL) and Et_2O (7 mL). The bomb was closed with a Teflon® seal. The mixture was stirred at room temperature for 24 hrs. The resulting solid in suspension was filtrated, washed with dichloromethane, HCl (12N), Et_2O and dried under vacuum to afford the desired product **8d** as a pale powder (575 mg, 1.53 mmol, 70% yield). MS (MALDI-TOF): calcd. for $\text{C}_{18}\text{H}_{30}\text{N}_4^+$ ($[\text{M}]^+$) 302.2, found 302.2. No ^1H NMR spectrum could be recorded owing to the poor stability of **8d** in solution.

Synthesis of N^1,N^5 -bis(3,4,5-trimethoxyphenyl)-2,5-diamino-1,4-benzoquinonediimine (2a): To a mixture of **8a** (200 mg, 0.37 mmol, 1 equiv.) in EtOH (20 mL) were added K_2CO_3 (100 mg, 0.72 mmol, 2 equiv.). The mixture was stirred at room temperature for 2 days. After evaporation of the solvent the resulting solid crude was washed with H_2O , Et_2O and dried under vacuum to afford the desired product **2a** as a red solid (120 mg, 0.26 mmol, 70 % yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.62 (br s, 4H, N-H), 6.27 (s, 4H, Ar-H), 5.95 (s, 1H, quinone-H), 5.71 (s, 1H, quinone-H), 3.64 (s, 12H, OCH_3), 3.58 ppm (s, 12H, OCH_3); HRMS (ESI-TOF): calcd. for $\text{C}_{24}\text{H}_{29}\text{N}_4\text{O}_6^+$ ($[\text{M}+\text{H}]^+$) 469.2082, found 469.2083.

Synthesis of N^1,N^5 -bis(4-tertbutylphenyl)-2,5-diamino-1,4-benzoquinonediimine (2b): To a mixture of **8b** (600 mg, 1.26 mmol, 1 equiv.) in EtOH (20 mL) were added K_2CO_3 (870 mg, 6.3 mmol, 5 equiv.). The mixture was stirred at room temperature for 1 day. After evaporation of the solvent the resulting solid was washed with H_2O , Et_2O and dried under vacuum to afford **2b** as a red powder (442 mg, 87 % yield); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.28 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 4H, Ar-H), 6.89 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 4H, Ar-H), 5.77 (s, 1H, quinone-H), 5.68 (s, 1H, quinone-H), 1.23 ppm (s, 18H, CH_3); HRMS (ESI-TOF): calcd. for $\text{C}_{26}\text{H}_{32}\text{N}_4^+$ ($[\text{M}+\text{H}]^+$) 401.2700, found 401.2700.

Synthesis of N^1,N^5 -bis(3,5-bis(trifluoromethyl)phenyl)-2,5-diamino-1,4-benzoquinonediimine (2c): To a mixture of **8c** (200 mg, 0.31 mmol, 1 equiv.) in EtOH (20 mL) were added K_2CO_3 (218 mg, 1.58 mmol, 5 equiv.). The mixture was stirred at room temperature for 5 days. After evaporation of the solvent the resulting solid was washed with H_2O , Et_2O and dried under vacuum to afford **2c** as a red powder (74 mg, 0.13 mmol, 41 % yield); ^1H NMR (400 MHz, CDCl_3): δ = 7.54 (s, 2H, Ar-H), 7.33 (s, 4H, Ar-H), 5.85 (s, 1H, quinone-H), 5.70 ppm (s, 1H, quinone-H); HRMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{13}\text{N}_4\text{F}_{12}^+$ ($[\text{M}+\text{H}]^+$) 561.0943, found 561.0946.

Synthesis of N^1,N^5 -biscyclohexyle-2,5-diamino-1,4-benzo-quinonediimine (2d): To a mixture of **8d** (100 mg, 0.27 mmol, 1 equiv.) in EtOH (20 mL) was added K_2CO_3 (147 mg, 1.1 mmol, 4 equiv.). The mixture was stirred at room temperature for 2 days. After evaporation of the solvent, the resulting solid was washed successively with H_2O and *n*-pentane before being dried under vacuum to afford **2d** as a brown powder (52 mg, 0.18 mmol, 65 % yield); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 9.15 (br s, 1H, N-H), 6.15 (br s, 1H, N-H), 5.85 (br s, 2H, N-H) 5.46 (s, 1H, quinone-H), 5.28 (s, 1H, quinone-H), 3.50 (m, 2H, N-CH), 3.23 (m, 2H, N-CH), 1.98-1.48 (m, 20H, CH_2), 1.48-1.10 ppm (m, 20H, CH_2); HRMS (ESI-TOF): calcd. for $\text{C}_{18}\text{H}_{28}\text{N}_4^+$ ($[\text{M}+\text{H}]^+$) 301.2387, found 301.2389.

Synthesis of N^1,N^5 -dioctyl-2,5-diamino-1,4-benzoquinone-diimine (2e): To a mixture of **8e** (40.0 mg, 0.093 mmol, 1 equiv.) in EtOH (10 mL) was added K_2CO_3 (51.5 mg, 0.372 mmol, 4 equiv.). The mixture was stirred at room temperature for 2 days. After evaporation of the solvent the resulting solid crude was washed with H_2O and dried under vacuum to afford **2e** as a brown oil (20.0 mg, 0.056 mmol, 60 % yield); 1H NMR (400 MHz, $DMSO-d_6$): δ = 9.16 (br s, 1H, N-H), 6.37 (br s, 1H, N-H), 5.84 (br s, 2H, N-H) 5.43 (s, 1H, quinone-H), 5.22 (s, 1H, quinone-H), 3.36 (m, 2H, $N-CH_2$), 3.02 (m, 2H, $N-CH_2$), 1.57 (m, 4H, CH_2), 1.42-1.0 (m, 20H, CH_2), 0.84 ppm (m, 6H, CH_3); HRMS (ESI-TOF): calcd. for $C_{22}H_{41}N_4^+$ ($[M+H]^+$) 361.3326, found 361.3328.

Synthesis of N^1,N^5 -bis(3,4,5-trimethoxyphenyl)- $N2,N4$ -dioctyl-2,5-diamino-1,4-benzoquinonediimine (4a):

From **8a**: To a mixture of **8a** (103 mg, 0.19 mmol, 1 equiv.) in MeOH (25 mL) was added *n*-octylamine (252 μ L, 1.52 mmol, 8 equiv.). The mixture was stirred at room temperature for 2 days. After evaporation of the solvent, the resulting crude product was dissolved with pentane. Insoluble compounds were filtered and the filtrate was evaporated to dryness. The crude product was purified on size exclusion chromatography column (Bio-BeadsTM S-X3 support, dichloromethane, length = 45 cm) to afford the desired product **4a** as a red oil (70 mg, 0.1 mmol, 52 % yield).

From **2a**: To a mixture of **2a** (50 mg, 0.107 mmol, 1 equiv.) in MeOH (25 mL) were added HCl 0.3 M (71 μ L, 0.02 mmol, 0.2 equiv.), *n*-octylamine (140 μ L, 0.856 mmol, 8 equiv.). The mixture was stirred at room temperature overnight. After evaporation of the solvent, the resulting crude product was dissolved in *n*-pentane. Insoluble compounds were filtered and the filtrate was evaporated to dryness. The crude product was purified on a size exclusion chromatography column (Bio-BeadsTM S-X3 support, dichloromethane, length = 45 cm) to give **4a** as a red oil (54 mg, 0.078 mmol, 73 % yield). 1H NMR (400 MHz, $CDCl_3$) δ = 7.31 (br s, 2H, N-H), 6.18 (s, 4H, Ar-H), 6.09 (s, 1H, quinone-H), 5.42 (s, 1H, quinone-H), 3.78 (s, 6H, OCH_3), 3.74 (s, 12H, OCH_3), 3.32 (t, $^3J_{HH}$ = 7.1 Hz, 4H, $N-CH_2$), 1.74 (q, $^3J_{HH}$ = 7.1 Hz, 4H, $CH_2-CH_2-CH_2$), 1.50-1.21 (m, 20H, CH_2), 0.89 ppm (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2-CH_3); HRMS (ESI-TOF): calcd. for $C_{40}H_{61}N_4O_6^+$ ($[M+H]^+$) 693.4586, found 692.4586.

Synthesis of N^1,N^5 -bis(3,4,5-trimethoxyphenyl)-2,5-diamino-1,4-benzoquinonediimine Pt complex (12): To a solution of **2a** (30 mg, 0.064 mmol, 1 equiv.) in dichloromethane (10 mL) were added $PtCl_2(COD)$ (50 mg, 0.34 mmol, 2.1 equiv.) and Et_3N (44 μ L, 0.32 mmol, 5 equiv.). The reaction was stirring overnight at room temperature. The solution was then evaporated to dryness under vacuum and the residue was taken up in Et_2O . The resulting solid in suspension was isolated by filtration and purified on size exclusion chromatography column (Bio-BeadsTM S-X3 support, dichloromethane, length = 45 cm) to afford the desired product **12** as a red solid (64 mg, 0.06 mmol, 94% yield); HRMS (ESI-TOF): calcd. for $C_{40}H_{49}N_4O_6Pt^+$ ($[M+H]^+$) 1071.2938, found 1071.2942. NMR data of **12** appeared poorly workable¹⁴ probably due to the presence of two isomers in solution (see SI) or the possible different hapticity of the cod ligands.²⁴

Synthesis of N^1,N^5 -bis(3,4,5-trimethoxyphenyl)-2,5-diamino-1,4-benzoquinonediimine Pt complex (13): To a suspension of **2a** (100 mg, 0.21 mmol, 1 equiv.) in *n*-heptane (20 mL) in a pressure bomb were added $Pt(acac)_2$ (41 mg, 0.1 mmol, 0.5 equiv.). The bomb was closed with a Teflon[®] seal. The mixture was stirred 150 °C for 20hrs. The resulting solid in suspension was filtrated, washed with Et_2O and dried under vacuum. The crude product was purified on a size exclusion chromatography column (Bio-BeadsTM S-X3 support, dichloromethane, length = 45 cm) to afford the desired product **13** as a purple solid (27 mg, 0.024 mmol, 23% yield); 1H NMR (400 MHz, $DMSO-d_6$): δ = 7.82 (br s, 2H, N-H), 6.92 (br s, 4H, N-H), 6.42 (s, 4H, Ar-H), 6.01 (s, 4H, Ar-H), 5.78 (s, 2H, quinone-H), 5.2 (s, 2H, quinone-H), 3.66 (s, 9H, OCH_3), 3.64 (s, 6H, OCH_3), 3.63 (s, 9H, OCH_3), 3.56 ppm (s, 6H, OCH_3); HRMS (ESI-TOF): calcd. for $C_{48}H_{55}N_8O_{12}Pt^+$ ($[M+H]^+$) 1130.3587, found 1130.3586.

Synthesis of 14: To a solution of **13** (15 mg, 0.013 mmol, 1 equiv.) in dichloromethane (10 mL) were added $PtCl_2(COD)$ (10 mg, 0.027mmol, 2.1 equiv.) and Et_3N (18 μ L, 0.13 mmol, 10 equiv.). The reaction was stirring overnight at room temperature. The solution was then evaporated to dryness under vacuum and the residue was taken up in Et_2O . The resulting solid in suspension was isolated by filtration and purified on a size exclusion chromatography column (Bio-BeadsTM S-X3 support, dichloromethane, length = 45 cm) to afford the desired product **14** as a blue solid (21 mg, 0.012 mmol, 91% yield); HRMS (ESI-TOF): calcd. for $C_{64}H_{76}N_8O_{12}Pt_3^{2+}$ ($[M+2H]^{2+}$) 867.2262, found 867.2262. NMR data of **14** appeared poorly workable¹⁴ probably due to the presence of two isomers in solution (see SI) or the possible different hapticity of the cod ligands.²⁴

Synthesis of $N1,N5$ -bis(3,4,5-trimethoxyphenyl)- $N2,N4$ -dioctyl-2,5-diamino-1,4-benzoquinonediimine $\{Ni(acac)\}_2$ complexe (15): To a solution of **4a** (20mg, 0.028 mmol, 1 equiv.) in THF (5 mL) were added $Ni(acac)_2$ in THF (5 mL). The reaction was stirring overnight at room temperature. After concentration, the residue was washed with pentane and the filtrate was concentrated under reduced pressure. The resulting solid was purified on size exclusion chromatography column (Bio-BeadsTM S-X3 support, dichloromethane, length = 45 cm) to afford the desired product **15** as a dark red solid (13.8 mg, 0.014 mmol, 62% yield); 1H NMR (400 MHz, $CDCl_3$): δ = 6.18 (s, 4H, Ar-H), 5.28 (s, 2H, Acac-H), 4.71 (s, 1H, quinone-H), 4.40(s, 1H, quinone-H), 3.69 (s, 12H, OCH_3), 3.68 (s, 6H, OCH_3), 2.39 (m, 4H, CH_2), 1.60 (s, 12H, Acac- CH_3), 1.53-1.42 (m, 4H, CH_2), 1.36-1.18 (m, 20H, CH_2) 0.89 (m, 6H, CH_3); HRMS (ESI-TOF): calcd. for $C_{50}H_{72}N_4O_{10}Ni_2Na^+$ ($[M+Na]^+$) 1027.3848, found 1027.3849.

Conclusions

In summary, we described the first N,N'-disubstituted QDIs **2a-e** in which the absence of substituents on one of the two amino-enamine subunits induces a specific reactivity, demonstrating the crucial role of the number of substituents on the reactivity of the corresponding QDIs. These new members of QDIs were used as new unhindered soluble ligands able to form with Ni(II) precursors a mixture of complexes with different lengths. If their isolation could not be achieved because of purification problems, an intense absorption band in the NIR region ($\lambda_{\text{max}} = 842 \text{ nm}$) could be observed. In the presence of the less reactive Pt(II) precursors, metal complexes with different M:L ratio (2:1, **12**; 1:2, **13**; and 3:2, **14**) could be isolated in good yields. Monoplatinum complex **13** appeared unique in that it revealed remarkable NIR absorption properties (*i.e.* up to 1000 nm) because of a "wave-type" delocalization pathway of the electrons, an exceptional feature. In addition, molecule **13** can be viewed as a new precursor of choice for metalation of its "terminal" coordination sites. In other words, ligands of type **2a** give access to complexes with unusual properties (**13** and **14**) that were not accessible previously from N,N',N'',N'''-tetrasubstituted **1**, paving the way to new investigations in coordination chemistry.²⁵ Furthermore, in contrast to their N,N',N'',N'''-tetrasubstituted analogues **1**, these new QDI ligands (**2a**) showed an extremely large pK_a difference ($\Delta\text{pK}_a \sim 8$) and an absorption up to the NIR region for the diprotonated species resulting from a modulation of the basic character of each imine. N,N'-disubstituted QDIs **2a-e** can be also considered as reagents of choice in organic synthesis through a transamination reaction that allowed the first isolation of a tetrasubstituted QDI ligand **4a** for which the fine-tuning of the electronic density on the nitrogen atoms has been rendered possible (alkyl and aryl substituents simultaneously). This study clearly demonstrates the major impact of the number of N-substituents on the properties of these 12 π electron quinones, a long known class of QDIs but never investigated previously on its N,N'-disubstituted form. Least, the combination of both redox properties of the transition metals (Ni, Pt) and ligands (**2**) in **12-15** should provide multiredox systems for functionalized materials and catalysts,²⁶⁻³² whereas the Pt(cod) units in **12** and **14** can be used as proton-reservoir for substrate bond activation as already observed on related complexes.²⁴

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