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Synthesis and electro-spectroelectrochemistry of ferrocenyl naphthaquinones

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ABSTRACT

A practical approach to ferrocenyl naphthaquinone derivatives involving thermal rearrangement of variously substituted 4-aryl-4-hydroxycyclobutenones was described. The reaction of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione with different aryl lithiums gave the corresponding 4-aryl-4-hydroxycyclobutenones, which were heated in *p*-xylene at reflux open to the air to yield ferrocenyl naphthaquinones. The redox chemistry of the ferrocenyl naphthaquinones was studied by electrochemical and in situ spectroelectrochemical techniques in CH_2Cl_2 solution and in CH_3CN solution with water, weak and strong acidic additives. Ferrocenyl naphthaquinones displayed reversible two reduction processes involving semiquinone radical anion (Fc–snq$^{\bullet-}$), dianion (Fc–nq^{2-}) species and a one-electron oxidation process based on the ferrocenium/ferrocene (Fc^{+}–nq/Fc–nq) couple in CH_2Cl_2. The redox reaction mechanism of the ferrocenyl naphthaquinones in the presence of the additives proceeded via hydrogen bonding or proton-coupled electron transfer. Effects of the substituents on the reduction potentials and intramolecular charge-transfer bands of ferrocenyl naphthaquinones were also discussed.

1. Introduction

In recent years, ferrocene and its derivatives have received considerable attention since they have found potential applications in the fields of asymmetric synthesis,[1] bioorganometallic chemistry,[2] and particularly in materials science.[3] Ferrocene has become one of the most preferred components of molecular electron transfer systems in artificial photosynthesis studies[4] and in the development of optoelectronic devices.[5] As an electron-donor unit having chemical versatility, thermal stability as well as a reversible electrochemical redox couple, ferrocene participates in electron transfer systems with various electron acceptors and redox-active species such as fullerene,[6] BODIPY,[7] porphyrins,[8] phthalocyanines,[9] and corroles.[10] Dithiafulvalene[11] and tetrathiafulvalene[12] derivatives of ferrocene have been reported as donor conducting materials for charge-transfer complexes. Moreover, ferrocene has been combined with good electron acceptor quinones covalently or by various spacers. Ferrocene–benzoquinone[13] and ferrocene–anthraquinone[14] donor–acceptor systems with or without a spacer are quite common. Both quinones and ferrocene exhibiting well-established reversible electrochemical redox couples are the most important and well-studied examples of an organic/organometallic redox system.[15] From a fundamental standpoint, these model molecules have played an important role in developing our current understanding of organic and organometallic redox chemistry.[16] Additionally, as remarkable electron donor–acceptor pairs, ferrocene, and quinones provide tunable redox potentials through judicious choice of substituents. Thus, coupling ferrocene and quinones intramolecularly would then offer interesting candidates for studying electron transfer reactions and optical properties.[17]

Electron transfer plays a pivotal role not only in chemical processes but also in biological redox processes that have tremendous relevance to our life, such as photosynthesis and respiration.[18] To understand the factors for controlling important electron-transfer processes in biological systems, electron-transfer dynamics between donor and acceptor molecules bound to proteins have been studied extensively.[19] Considering the redox chemistry of quinone-based couples, these species are closely related to biological processes as electron-proton transfer agents in the oxidative phosphorylation of ADT to ATP, or photosynthesis, which themselves are directly affected the by acid–base properties of quinone, semiquinone, and hydroquinone species.[20]

It has been determined that the electrochemical behavior of quinone is strongly influenced by environmental conditions that regulate the potentials and reaction pathways of the reduced/oxidized species appearing in a proton-coupled electron transfer.[15f,g,20a,21] A deep insight into the redox processes of quinones can be gained by performing detailed studies on the electrochemical behaviors of quinones, particularly, in non-aqueous media using aprotic solvents, which are useful in mimicking the non-polar environments in the cell where many biological electron-transfer processes occur.[20a] In dry, neutral and aprotic media, quinones

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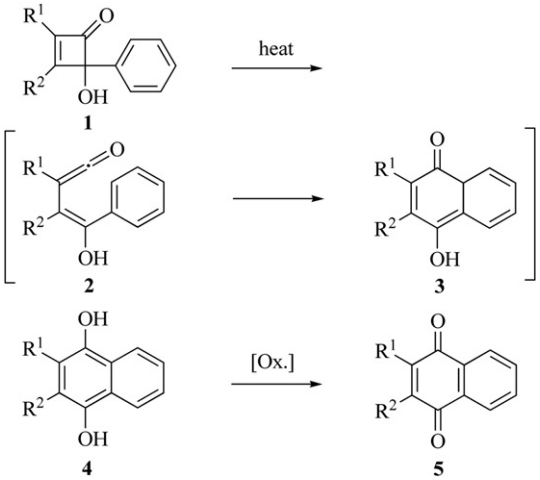
typically show two cathodic chemically reversible waves, which correspond to the formation of the semiquinone radical anion ($sq^{\bullet -}$) and dianion (q^{2-}), respectively.[15f] The potentials of these reductions depend on several parameters, such as the solvent, supporting electrolyte and electrode material as well as the electron-withdrawing or -donating substituents appended on the quinone unit.[15f,20a,21a] The course of electroreduction for quinones is remarkably complex in the acidic medium as described in numerous studies.[15d,f,g,20a,21,22] Several recent studies reported hydrogen bonding and protonation effects on the redox behavior of quinones through electrochemical investigations.[15d,20a,23] Hydrogen bonds are particularly important for biological systems where they provide essential recognition, structural, and control elements needed to coordinate and run the complex molecular machinery required for life.[20a,23a,24] Moreover, the hydrogen bonding can be viewed as a first step toward proton transfer.[15d,20a] The electrochemical and spectroelectrochemical investigations on the quinone redox system involving the electron transfer coupled with the hydrogen bonding give much information concerning the effect of molecular structure and environment on these basic processes.[23,25] It is well-known that the combination of electrochemical and spectroelectrochemical methods provides a powerful tool to reveal the complementary nature of the molecular structure. Moreover, these methods supply detailed electrochemical information to clarify mechanism of electron transfer reactions.[26]

In this study, we have devoted our interests to the synthesis of new ferrocenyl naphthaquinone derivatives via a well-established regiospecific method, which offers an easy access to highly substituted quinones.[27] Generally, the method entails thermal rearrangements of reactive 4-alkenyl-, 4-(aryl or heteroaryl)-4-hydroxycyclobutenones, such as **1**, to the naphthaquinone derivative **5** after the oxidation of the initially formed hydroquinone **4** (Scheme 1). We employed this method, for the first time, to achieve various ferrocenyl naphthaquinones (**10a**–**k**, **11g**, and **13**) starting from 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**) and aryl lithiums **7a**–**k**. The method has been applied before for the synthesis of ferrocenyl benzoquinones by Zora et al.[13c] However, to the best of our knowledge, only three ferrocenyl naphthaquinone derivatives have been prepared by the reaction of Fischer-type chromium carbene complexes with ethynylferrocene.[28] Here, we have also presented an electrochemical approach to the mechanistic study of hydrogen bonding and proton-coupled electron transfer of ferrocenyl naphthaquinones in non-aqueous solutions in the absence and presence of acidic additives.

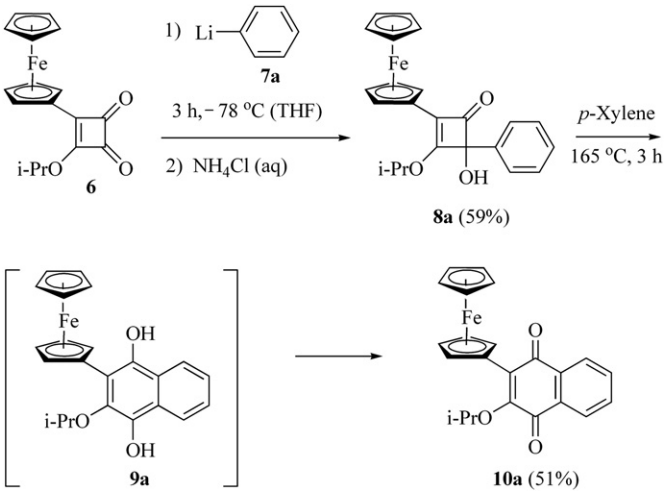


Scheme 1. Thermal rearrangement of 4-aryl-4-hydroxycyclobutenone **1** to the naphthaquinone derivative **5** (R^1, R^2=alkyl, aryl, heteroaryl, alkoxy, etc.).

2. Results and discussion

2.1. Synthesis of ferrocenyl naphthaquinone derivatives

We initially attempted the synthesis of ferrocenyl-substituted 4-hydroxy-4-phenylcyclobutenone **8a** by the reaction of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**)[13c,29] with phenyllithium (**7a**) according to well-documented literature procedures.[27,30] Surprisingly, thermolysis of the isolated ferrocenyl-substituted 4-hydroxy-4-phenylcyclobutenone (**8a**), even under a nitrogen atmosphere, furnished directly the oxidized product ferrocenyl naphthaquinone **10a** in 51% yield instead of a hydroquinone derivative **9a** (Scheme 2). However, isolating the 4-hydroxycyclobutenone **8a** by column chromatography was quite tedious and we noticed that the alcohol **8a** was prone to decompose slowly when it was stored, particularly at rt.

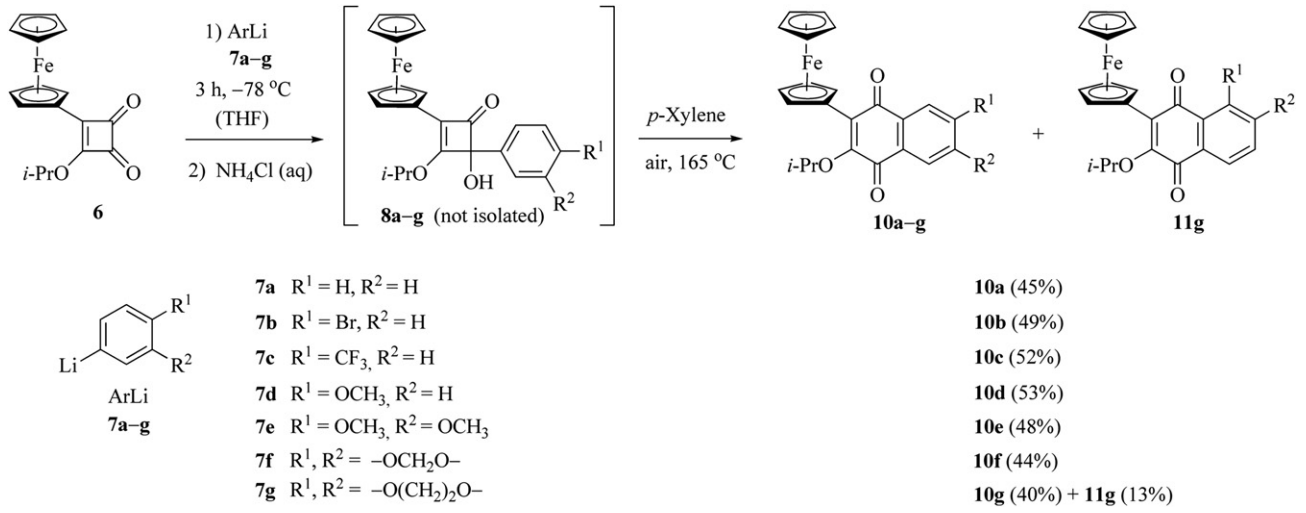


Scheme 2. Synthesis of ferrocenyl naphthaquinone **10a** via a thermal rearrangement of the isolated 4-hydroxy-4-cyclobutenone intermediate **8a** in *p*-xylene.

A more practical synthetic approach to the ferrocenyl naphthaquinone derivative **10a** was achieved without isolation and purification of ferrocenyl-substituted 4-hydroxy-4-phenylcyclobutenone **8a**. The crude material obtained by treatment of a THF solution of **6** at −78 °C with phenyllithium (**7a**), followed by an ammonium chloride quench, was directly dissolved in *p*-xylene and the resulting solution was heated at reflux open to the air to promote oxidation of intermediate hydroquinone **9a** (Scheme 3). During heating, the color of the solution slowly turned deep green and the color change persisted with disappearance of the ferrocenyl-substituted 4-hydroxy-4-phenylcyclobutenone **8a** in 4 h. After evaporation of *p*-xylene and column chromatography, the ferrocenyl naphthaquinone **10a** was obtained in 45% overall yield from 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**).

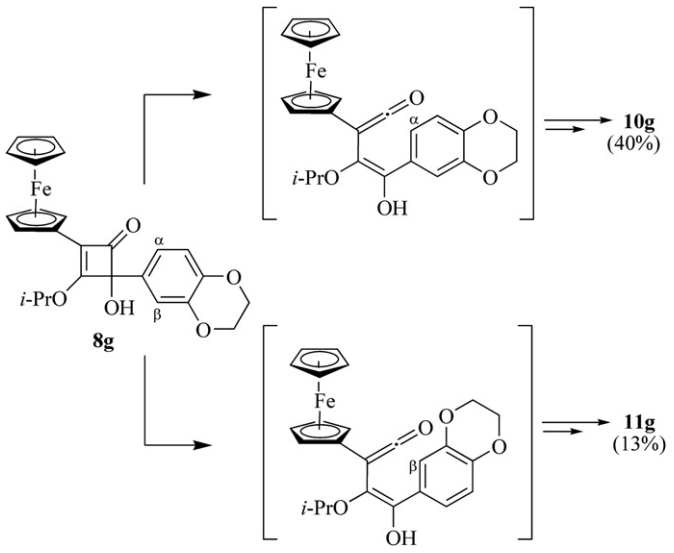
To investigate the scope and limitations of this short synthetic approach to ferrocenyl naphthaquinone derivatives, we performed the reaction of cyclobutenedione **6** with differently substituted aryl lithiums **7a**–**g**, which were in situ prepared (except for **7a**) by the reaction of a slight excess of *n*-BuLi with the corresponding aryl bromides in dry THF at −78 °C. The thermolyses of crude mixtures of 4-aryl-4-hydroxycyclobutenones **8a**–**g** were completed within 4 h and gave the ferrocenyl naphthaquinone derivatives **10a**–**g** and **11g** in moderate yields (40–53%). In all attempts, a ferrocenyl hydroquinone derivative of type **9a** was not observed (Scheme 3).

Although the thermal rearrangements of 4-aryl-4-hydroxycyclobutenones (**8e**–**g**) are open to give two regioisomeric naphthaquinones via ring closure at two different positions of aryl groups, for example, α or β in **8g**, only the thermolysis of the cyclobutenone **8g** gave the angularly-fused ferrocenyl naphthaquinone derivative



Scheme 3. Synthesis of ferrocenyl naphthaquinone derivatives **10a**–**g** and **11g** via a reaction of ferrocenyl cyclobutenedione **6** with aryl lithiums **7a**–**g** followed by open air thermolyses of the intermediate 4-hydroxy-4-cyclobutenone intermediates **8a**–**g**.

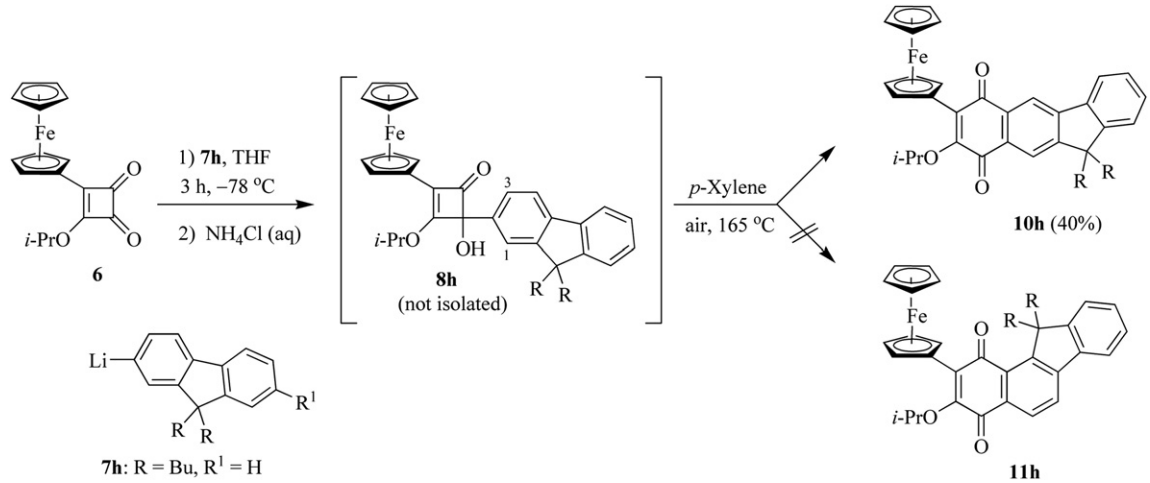
11g in 13% yield along with the linearly-fused derivative **10g** in 40% yield (Scheme 4).



Scheme 4. Formation of regioisomeric ferrocenyl naphthaquinone derivatives **10g** and **11g** via a ring closure at two different position (α and β) of the aryl group.

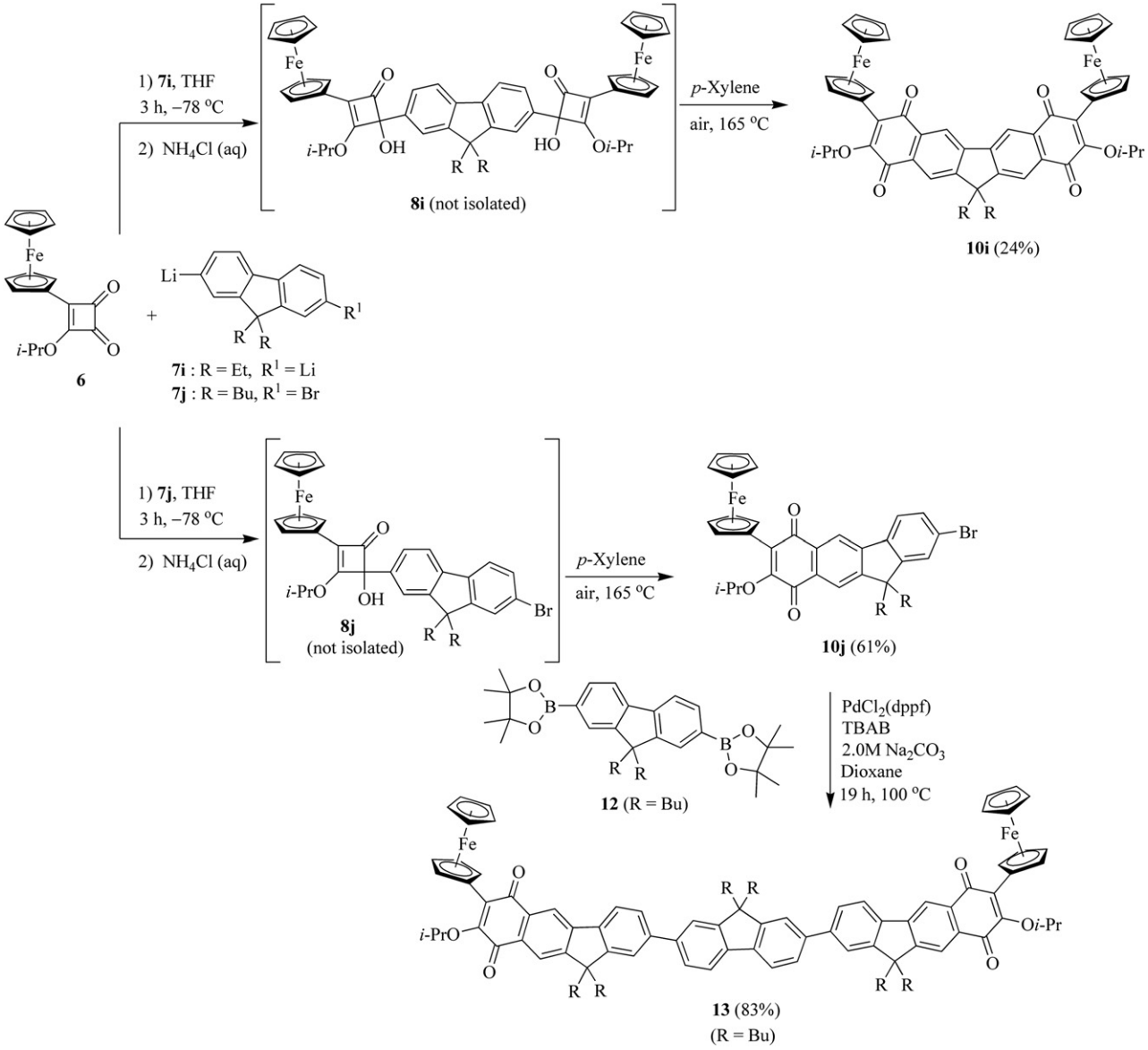
To extend the scope of this study even further, we aimed to synthesize structurally more complex ferrocenyl naphthaquinone derivatives. The reaction of cyclobutenedione **6** with 2-lithio-9,9-dibutyl-fluorene (**7h**), followed by thermal rearrangement of the intermediate hydroxycyclobutenone **8h** via a ring closure at the 3-position of the fluorenyl moiety furnished ferrocenyl naphthaquinone **10h** in 40% yield as a single product. A possible angularly-fused regioisomer **11h**, which would arise upon ring closure at the 1-position of the fluorenyl group, was not observed. Therefore, this result implies that, alkyl groups on the fluorene moiety play a pivotal role on the regioselective formation of the product **10h** by suppressing ring closure at the 1-position (Scheme 5).

In order to add another dimension to the scope of this study, we turned our attention to the synthesis of naphthaquinones with two ferrocenyl units since bimetallic systems containing an organic π-conjugated backbone with redox-active sites have recently emerged as new materials possessing unusual optoelectronic properties. For example, ferrocenyl end-capped fluorene-containing molecules have attracted much interest.[4d,31] Thus, in this course, we synthesized the linearly-fused ferrocenyl naphthaquinones **10i** albeit in 24% yield via a reaction of 2 equiv **6** with 2,7-dilithio-9,9-diethyl-fluorene (**7i**), followed by heating the initially formed hydroxycyclobutenone **8i**. Similarly, when the related sequence was initiated with the reaction of cyclobutenedione **6** and mono-lithiated bromofluorene derivative **7j**, ferrocenyl naphthaquinone **10j** was



Scheme 5. The reaction of cyclobutenedione **6** with 2-lithio-9,9-dibutyl-fluorene (**7h**) followed by thermal rearrangement of the intermediate hydroxycyclobutenone **8h** via a ring closure at the 3-position; regioselective formation of linearly-fused ferrocenyl naphthaquinone **10h**.

accessed in 61% yield. Ferrocenyl naphthaquinone (2 equiv) **10j** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dibutylfluorene (**12**) in a mixture of dioxane and 2.0 M aqueous solution of Na_2CO_3 and tetrabutylammonium bromide (TBAB), were treated with a palladium catalyst [$PdCl_2$(dppf): [1,1′-bis(diphenylphosphino)ferrocene]dichloropalla-dium(II)] for 19 h to furnish the target product **13** containing three fluorene moieties (Scheme 6).



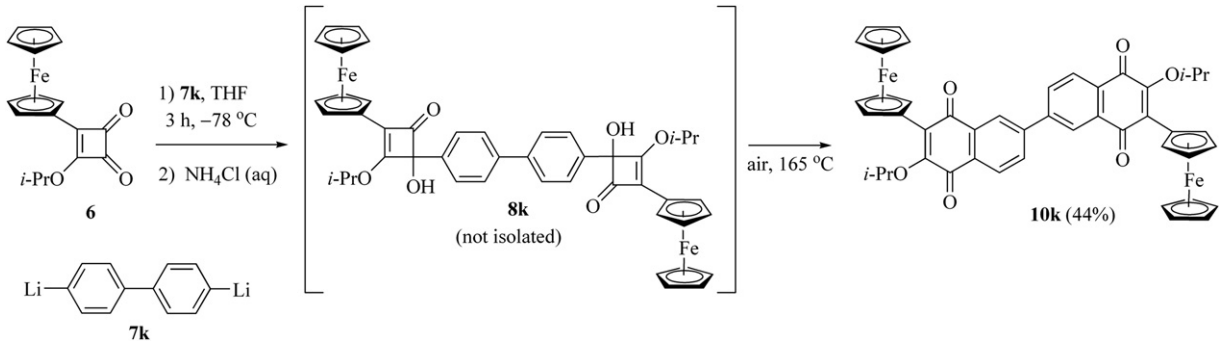
Scheme 6. Synthesis of oligocyclic ferrocenyl naphthaquinone derivatives **10i–j** and the formation of compound **13** by Suzuki-cross-coupling reaction of ferrocenyl naphthaquinone **10j** with diboronic ester **12**.

In addition to these achievements, a bis(ferrocenyl naphthaquinone) derivative **10k** was obtained in 44% yield by the reaction of ferrocenyl cyclobutenedione **6** with 4,4′-dilithiobiphenyl (**7k**) and subsequent thermolysis of the intermediate hydroxycylobutenones **8k** in *p*-xylene for 4 h (Scheme 7).

2.2. Electronic spectra of ferrocenyl naphthaquinone derivatives

Electronic spectra of the ferrocenyl naphthaquinone derivatives **10a–k**, **11g**, and **13** have been recorded in the 200–1100 nm range in CH_2Cl_2 solution and their corresponding data were listed in Table 1. All ferrocenyl naphthaquinones **10a–k**, **11g**, and **13** showed several absorptions in the visible and ultraviolet region. Examples of representative UV–vis spectra of **10b** (blue line), **10c** (magenta line), **10e** (red line), **10j** (green line), and **14**[32] (black dash line) (used as a reference molecule in this study) were given in Fig. 1.

The spectrum of **14** was dominated by a high intensity band at 252 nm and two moderate intensity bands at 333 and 408 nm, which were typical for naphthaquinone (n, $\pi \rightarrow \pi^*$) transitions.[33] In the spectra of the ferrocenyl naphthaquinones **10b**, **10c**, **10e**, and **10j**, the transition bands appeared at 723, 740, 687, and 699 nm, respectively, which indicated clearly an intramolecular charge-transfer between the ferrocenyl donor and naphthaquinonyl acceptor centers [e_π (HOMO–Fc)$\rightarrow e^*_\pi$ (LUMO–nq)] (Fig. 1 and Table 1). These transitions were responsible for the green color of the ferrocenyl naphthaquinones **10a–k**, **11g**, and **13**. The assignment is analogous to the previously well-characterized charge-transfer bands of ferrocene–DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) [e_π (HOMO–Fc)$\rightarrow e^*_\pi$ (LUMO–DDQ)] and ferrocene–benzoquinone [e_π (HOMO–Fc)$\rightarrow e^*_\pi$ (LUMO–q) donor–acceptor dyads.[17a,34] These bands disappeared upon one-electron oxidation of the ferrocene center or one-electron reduction of the naphthaquinone center, (see



Scheme 7. Synthesis of bis(ferrocenyl naphthaquinone) derivative **10k** via a reaction of ferrocenyl cyclobutenedione **6** with 4,4′-dilithiobiphenyl (**7k**) followed by open air thermolysis of the intermediate 4-hydroxy-4-cyclobutenone intermediate **8k**.

Table 1
The redox properties and UV–vis absorptions of the ferrocenyl naphthaquinones

Fc–nq	Fc–snq$^{\bullet-}$/Fc–nq^{-2} [a]$E_{1/2}$ [b](V) [c](ΔE_p)	Fc–nq/Fc–snq$^{\bullet-}$ [a]$E_{1/2}$ [b](V) [c](ΔE_p)	Fc^{+}–nq/Fc–nq [a]$E_{1/2}$ [b](V) [c](ΔE_p)	[d1]ΔE_p (V)	[e2]ΔE_p(V)	I_a/I_c (Fc^{+}–nq/Fc–nq)	I_c/I_a (Fc–nq/Fc–snq$^{\bullet-}$)	λ_{max}/nm (log ϵ) (n, $\pi\rightarrow\pi^*$)	$^{CT}\lambda_{max}$/nm (log ϵ) (HOMO→LUMO) ($e_\pi\rightarrow e^*_\pi$)
10a	−1.26 (0.17)	−0.78 (0.12)	0.58 (0.11)	1.36	0.48	1.05	1.07	255 (4.44) 333 (3.90) 408 (3.63)	693 (3.36)
10b	−1.24 (0.18)	−0.69 (0.12)	0.59 (0.12)	1.28	0.55	1.01	1.05	263 (4.56) 336 (3.99) 416 (3.74)	723 (3.51)
10c	−1.17 (0.12)	−0.63 (0.09)	0.58 (0.09)	1.21	0.54	0.99	1.01	260 (4.58) 325 (4.09) 411 (3.88)	740 (3.56)
10d	−1.33 (0.24)	−0.84 (0.14)	0.57 (0.14)	1.41	0.49	1.01	1.02	271 (4.44) 349 (3.99) 420 (3.48)	681 (3.28)
10e	−1.36 (0.21)	−0.84 (0.14)	0.56 (0.13)	1.40	0.52	1.01	1.02	280 (4.45) 345 (4.13) 436 (3.1)	687 (3.24)
10f	−1.32 (0.31)	−0.80 (0.17)	0.57 (0.17)	1.37	0.52	1.02	1.03	279 (4.52) 344 (4.13) 434 (3.04)	691 (3.28)
10g	−1.31 (0.34)	−0.80 (0.20)	0.59 (0.19)	1.39	0.51	1.00	1.12	284 (4.66) 340 (4.31) 430 (3.56)	677 (3.42)
10h	−1.32 (0.31)	−0.82 (0.15)	0.58 (0.21)	1.40	0.50	1.01	1.11	295 (4.51) 344 (4.02) 436 (3.47)	695 (3.16)
10i	−1.41 (0.17)	−0.76 (0.13); −0.87 (0.13)	0.58 (0.19)	1.34	0.54	1.08	1.01	302 (4.83) 427 (3.94)	713 (3.61)
10j	−1.33 (0.22)	−0.81 (0.14)	0.57 (0.14)	1.38	0.52	0.98	1.32	292 (4.63) 369 (3.98) 436 (3.67)	699 (3.36)
10k	−1.34 (0.30)	−0.72; −0.80	0.59 (0.14)	1.31	0.54	1.03	1.03	280 (4.77) 353 (4.35) 425 (3.96)	720 (3.62)
11g	−1.44 (0.26)	−0.91 (0.12)	0.56 (0.12)	1.47	0.53	1.05	1.06	275 (4.45) 315 (4.25) 400 (3.94)	657 (3.36)
13		−0.81 (0.12)	0.56 (0.12)	1.37		0.98	1.08	284 (4.19) 350 (4.49) 460 (3.85)	696 (3.22)
[f]**14**	−1.27 (0.21)	−0.76 (0.11)			0.51		0.95	252 (4.71) 333 (3.85) 408 (3.44)	

[a] $E_{1/2}=E_{pc}+E_{pa}/2$.
[b] In V versus Ag/AgCl (3 M NaCl) measured by cyclic voltammetry.
[c] $\Delta E_p=|E_{pc}-E_{pa}|$.
[d] $^1\Delta E_p=E_{1/2}(Fc^{+}–nq/Fc–nq)-E_{1/2}(Fc–nq/Fc–snq^{\bullet-})$.
[e] $^2\Delta E_p=E_{1/2}(Fc–nq/Fc–snq^{\bullet-})-E_{1/2}(Fc–nq^{\bullet-}/Fc–nq^{2-})$.
[f] Compound **14**: 2,3-diisopropoxy-1,4-naphthaquinone (nq) (used as a reference molecule in this study). Conditions: 3.75×10^{-3} M in dichloromethane with 0.1 M n-Bu_4NClO_4 as support electrolyte; working electrode, Pt disc electrode (1.6 mm diameter); counter electrode, Pt wire; reference electrode, Ag/AgCl (3 M NaCl); For the ferrocene, $E_{1/2}$ of Fc^{+}/Fc=0.53 V (ΔE_p=0.085 V) at the scan rate of 0.10 V s^{-1}; $c=5\times10^{-5}$ M in dichloromethane for UV–vis measurement.

the electrochemistry section for more details). The existence of intramolecular charge-transfer transitions with lower energy was also evidenced by the solvatochromic behavior of **10b**. The electronic spectra of **10b** were conducted in several solvents having different solvating capabilities. The lower energy band shifted to higher energy in more highly solvating solvents, whereas the higher energy bands in the UV region showed little change in energy with solvent [Supplementary data; Fig. S40 represents a plot of band wavelength against Reichardt's overall solvation scale parameter $E_T(30)$].[35] As expected, the electron-withdrawing and electron-donating substituents on the naphthaquinone moieties shifted the charge-transfer bands to lower and higher energies, respectively (Fig. 1 and Table 1). The charge-transfer band was highly shifted toward lower energy (740 nm) in the case of **10c** bearing a strong electron-withdrawing trifluoromethyl group. In addition, the position of the substituents on the naphthaquinone unit affected the energy of charge-transfer transitions. For example, the related bands for the linearly-fused **10g** and the angularly-fused **11g** ferrocenyl naphthaquinones (see Scheme 3) were observed at 677 and 657 nm, respectively. The 20 nm-shift to higher energy was probably due to a close interaction of the weak-electron donating dioxine group and the quinone moiety in **11g**. On the other hand, the charge-transfer bands for **10i** and **10k** were observed at 713 and 720 nm, respectively. The tendency of shifting to lower energies was probably caused by increasing effective π-conjugation between the ferrocene–quinone redox-active centers in these structures **10i** and **10k**. The maximum absorption wavelengths of the intramolecular charge-transfer displayed a good agreement with the difference in half-wave potentials of the

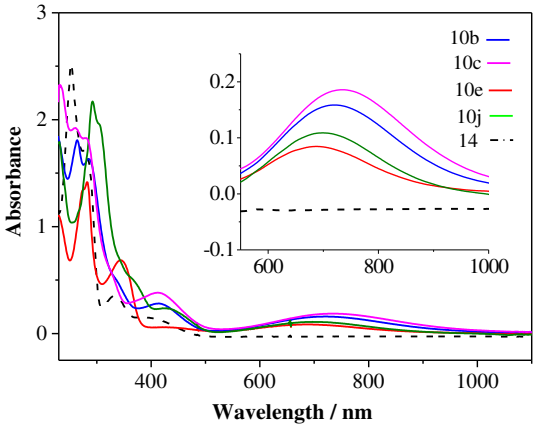


Fig. 1. UV–vis spectra of **10b** (blue line), **10c** (magenta line), **10e** (red line), **10j** (green line) and **14** (black dash line) in CH_2Cl_2 at rt. The inset shows charge-transfer bands. $c=5\times10^{-5}$ M.

oxidation and first reduction processes [$^{1}\Delta E_p = E_{1/2}(Fc^{+}-nq/Fc-nq) - E_{1/2}(Fc-nq/Fc-snq^{\bullet -})$] of the ferrocenyl naphthaquinone derivatives **10a**–**k** and **11g**, and is discussed in the electrochemistry section in more detail.

2.3. Electrochemistry and spectroelectrochemistry of ferrocenyl naphthaquinone derivatives

The electrochemical properties of the ferrocenyl naphthaquinones **10a**–**k**, **11g**, **13**, and the naphthaquinone **14** were investigated using cyclic voltammetry in CH_2Cl_2 and CH_3CN containing 0.1 M tetra-*n*-butylammonium perchlorate (*n*-Bu_4NClO_4) as supporting electrolyte. The redox potential data obtained in this work were gathered in Table 1. Cyclic voltammograms (CVs) of **10a** (black line) and **14** (red dash line) are shown in Fig. 2a.

The naphthaquinone **14** underwent a chemically reversible one-electron reduction process to form the semiquinone radical anion and displayed a chemically reversible one-electron oxidation process corresponding to the ferrocenium/ferrocene ($Fc^{+}-nq/Fc-nq$) couple at $E_{1/2}$=0.58 V (ΔE_p=0.11 V, I_{pa}/I_{pc}=1.05). Scheme 8 (by blue double arrows) summarizes the electrochemical pathways for the ferrocenyl naphthaquinones **10a**–**g** in non-aqueous media, which are also applicable for **10h**–**k**, **11g**, and **13**.

For the ferrocene, under our experimental conditions, $E_{1/2}$ of Fc^{+}/Fc was calculated as $E_{1/2}$=0.53 V (ΔE_p=0.085 V) at a scan rate of 0.10 V^{-1}, which can be used as a criterion for electrochemical reversibility.[36] The CVs in Fig. 2a illustrate that the anodic peak current appearing for the second reduction process is smaller than the current for the first reduction process. This can be attributed to a complexation reaction between the dianion (q^{2-}) and the neutral state of the quinone (q).[15d] The redox processes of the ferrocenyl naphthaquinone derivatives **10a**–**k**, **11g**, and **13** were examined as a function of potential scan rate in order to ascertain the mode of mass transport. The cathodic and anodic currents for the oxidation

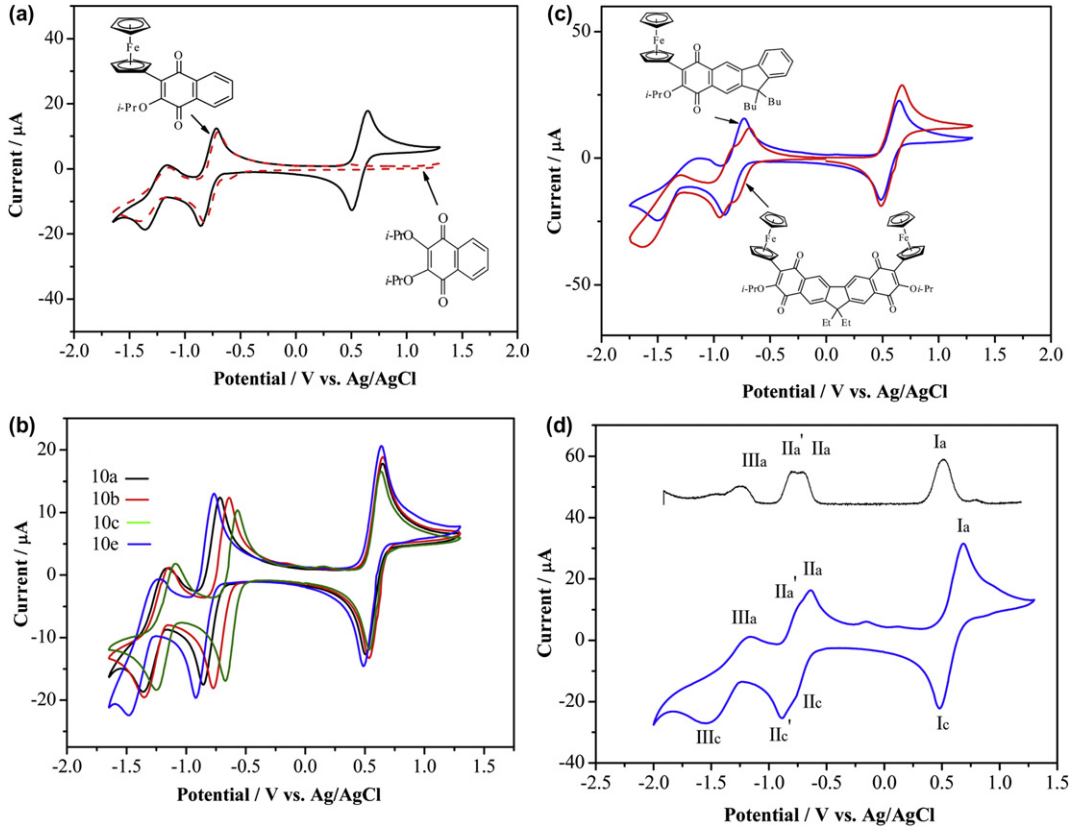
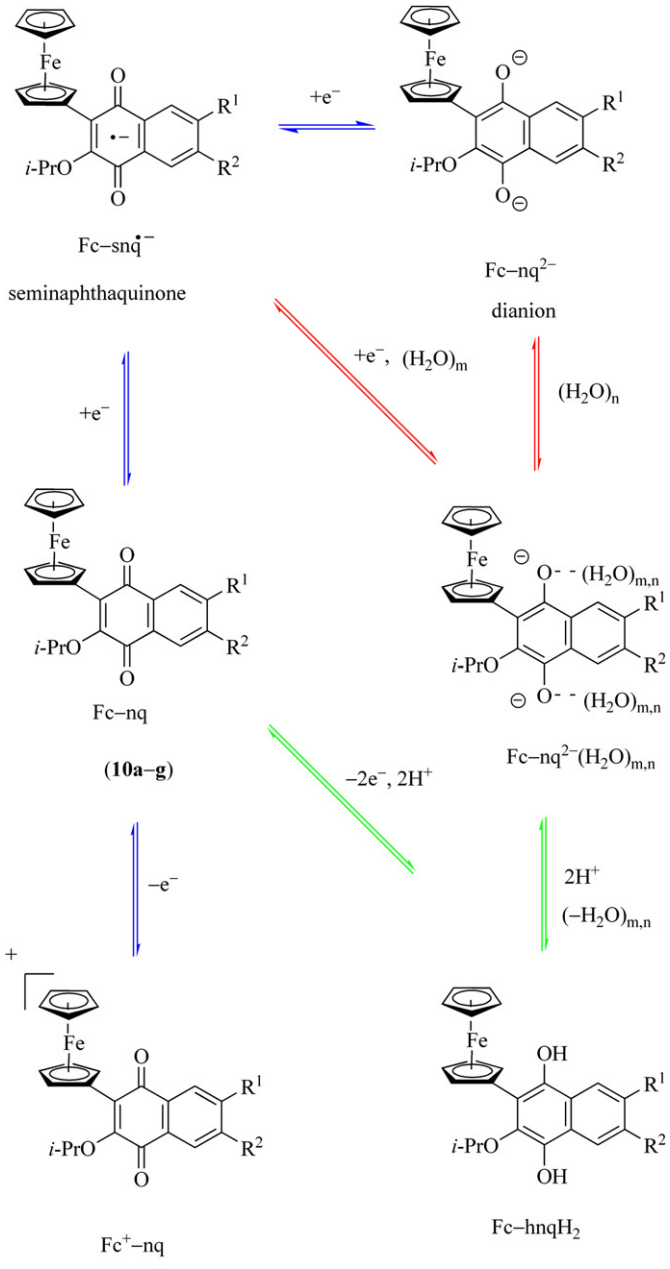


Fig. 2. Cyclic voltammograms of (a) **10a** (black line) and **14** (red dash line); (b) **10a** (black line); **10b** (red line), **10c** (green line), and **10e** (blue line); (c) **10h** (blue line) and **10i** (red line); (d) **10k** (blue line) in CH_2Cl_2 solution containing 0.1 M *n*-Bu_4NClO_4. Scan rates=0.10 V s^{-1}. Inset (black line) in (d) represents Differential pulse voltammogram (DPV) of **10k**. Scan rate=0.02 V s^{-1}, pulse PH/PW=0.025 V; step height=2.00 mV; step time: 100.0 ms. Working electrode: platinum disk electrode (1.6 mm diameter), c=3.75×10^{-3} M.

($Fc-snq^{\bullet -}$) at $E_{1/2}$ (half-wave potential)=−0.76 V [ΔE_p (the anodic to cathodic peak-to-peak separation)=0.11 V, I_{pc}/I_{pa} (the anodic–cathodic peak ratio)=0.95], which was further reduced by one electron at more negative potential (a quasi-reversible process at $E_{1/2}$=−1.27 V; ΔE_p=0.21 V) to form the dianion ($Fc-nq^{2-}$) species at a scan rate of 0.10 V s^{-1}. These results are similar to typical cyclic voltammograms of benzoquinone and naphthaquinone derivatives in aprotic organic solvents without acidic additives.[15d,f,22c,e,f,23a] The difference between the half-wave potentials of the first and second reduction processes [$^{2}\Delta E_p = E_{1/2}(nq/nq^{\bullet -}) - E_{1/2}(snq^{\bullet -}/nq^{2-})$] for **14** was 0.51 V, which was in accord with the those of the ferrocenyl naphthaquinones **10a**–**k**, **11g**, and **13** studied in this work (see Table 1). The ferrocenyl naphthaquinone **10a** exhibited two reduction processes, which had almost the same waves as **14** (Fig. 2a) and reduction couples in CH_2Cl_2 increased in a direct proportion to the square root of the scan rates between 0.05 and 1.0 V s^{-1}. This implied that these redox reactions were diffusion controlled[36] [Supplementary data; Fig. S41 represents CVs of **10a** at various scan rates (0.05–1.0 V s^{-1})]. Fig. 2b shows CVs obtained for **10a** (black line), **10b** (red line), **10c** (green line), and **10e** (blue line) under the same experimental conditions. The general feature of the CVs for **10b**, **10c** and **10e** was similar to that observed for **10a** discussed in details above, and their corresponding redox potential data are given Table 1. The $E_{1/2}$ of the first reduction of **10e**, **10b**, and **10c** were located at $E_{1/2}$=−0.84, −0.69, and −0.63 V, respectively, which were shifted to the more or less negative potentials as compared to that of **10a** ($E_{1/2}$=−0.78 V). The change in their redox potentials was caused by the effect of strong electron-donor methoxy and electron-



Scheme 8. The electrochemical reduction and oxidation mechanism for the ferrocenyl naphthaquinone derivatives in non-aqueous medium (the pathways indicated blue double arrows), after addition of weak acid (AcOH), (the pathways indicated diagonal green double arrows), and water (the pathways indicated red double arrows) followed strong acid (TFA), (the pathways indicated green double arrows) into the solution of CH_3CN.

withdrawing bromo and trifluoromethyl substituents on the 6,7 positions of the naphthaquinone core. Similar behavior was also observed for the second reduction processes. However, the oxidation processes corresponding to the Fc^+–nq/Fc–nq couple for the ferrocenyl naphthaquinones **10a**–**k**, **11g** and **13** displayed a similar value of $E_{1/2}$ (0.56–0.59 V), and a little change in $E_{1/2}$ values compared to that of ferrocene molecule ($E_{1/2}$ of Fc^+/Fc=0.53 V). This unexpected observation implied that the oxidation potential of the ferrocene electroactive center was not shifted to the positive potential by the acceptor naphthaquinone moiety. Similar behavior was reported in the literature where the oxidation potential of the Fc^+/Fc couple (0.60 V) observed for 1-ferrocenylanthraquinone, directly linked acceptor–donor units, showed only a slight anodic shift compared to that of the ferrocene molecule (0.55 V) in CH_2Cl_2.[37] The difference between the half-wave potentials of the oxidation and first reduction processes [$^1\Delta E_p = E_{1/2}(Fc^+–nq/Fc–nq) – E_{1/2}(Fc–nq/Fc–snq^{\bullet-})$], relating to the energy of the intramolecular charge-transfer transition between the ferrocenyl donor and naphthaquinonyl acceptor centers [e_π (HOMO–Fc)→e^*_π (LUMO–nq)], was ranged between 1.21 and 1.47 V according to substitution pattern. The $^1\Delta E_p$ values showed a good agreement with the maximum absorption wavelengths of the intramolecular charge-transfer. Fig. 2c shows the CVs of **10h** (blue dot line) and **10i** (red line). Similar to the ferrocenyl naphthaquinones **10a**–**g**, **11g**, the ferrocenyl naphthaquinone **10h** bearing a conjugated aromatic unit exhibited two chemically reversible reduction and one oxidation processes. On the other hand, the structures involving covalently-linked two ferrocenyl naphthaquinone units, **10i** and **10k**, displayed reduction processes corresponding to the semiquinone radical anion ($Fc–snq^{\bullet-}$) of the two naphthaquinone electrochemical centers as two separated waves accompanied with two electrons. Interestingly, similar behavior was not determined for the oxidation

processes of **10i** and **10k**. In these oxidation processes, the unit wave arising from the Fc^{+}–nq/Fc–nq couple occurred at the same potential with the ferrocenyl naphthaquinone derivatives **10a**–**h**, **11g**. Fig. 2d shows CV of **10k** (blue line), which is similar to that of **10i**, and the inset presents differential pulse voltammogram (DPV, black line) for **10k** where the first reduction processes are clearly differentiated as IIa and IIa' waves.

The spectroelectrochemical behavior of the ferrocenyl naphthaquinones was investigated using an in situ spectroelectrochemical technique including chronoamperometry and UV–vis spectroscopy in CH_3CN solution containing 0.2 M n-Bu_4NClO_4. The UV–vis spectral changes for the reduced and oxidized species of the corresponding derivatives were obtained in a thin-layer cell during applied potentials. The convenient applied potentials values for an in situ spectroelectrochemical experiment were determined for each process by taking CVs of the complexes in the thin-layer cell. Time-resolved UV–vis spectral changes of **10e** during the first reduction process at E_{app} (applied potential)=−1.15 V were depicted in Fig. 3a.

The spectra of the reduced species corresponding to the semiquinone radical anion (Fc–$snq^{\bullet -}$) showed well-defined isosbestic

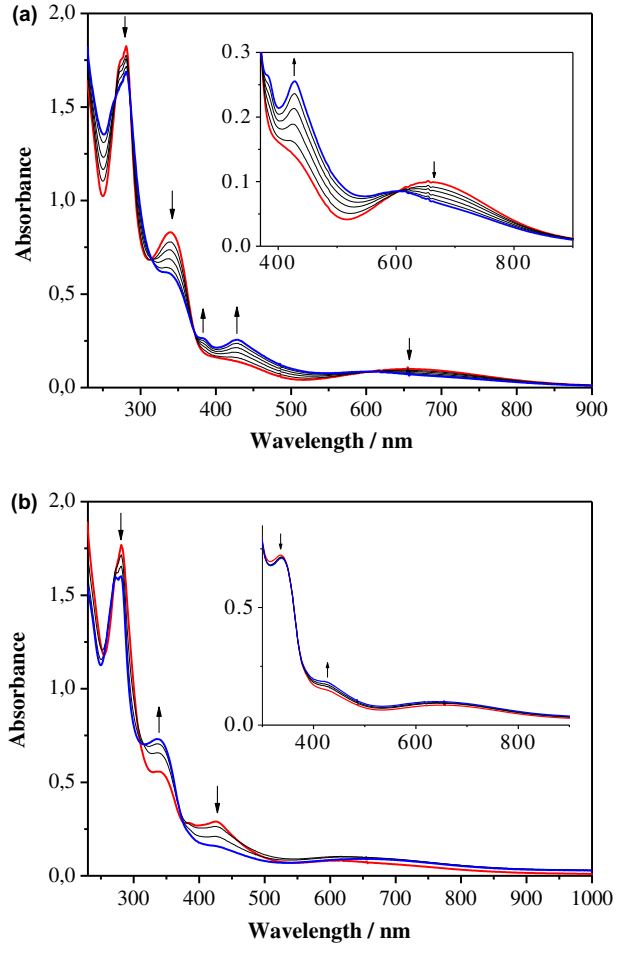


Fig. 3. Time-resolved UV–vis spectral changes of (a) **10e** during the first reduction at E_{app}=−1.15 V (b) **10e** during the second reduction at E_{app}=−1.75 V in CH_3CN solution containing 0.2 M n-Bu_4NClO_4. Arrows mark the direction of absorbance change.

points observed at 267, 312, 370, and 600 nm. This confirmed that the electrode reaction proceeded in a quantitative fashion and the absence of any coupled chemistry (Fig. 3a).[26a,b,d,f] The original spectrum of the neutral form (red line) showed several changes in intensity and band position resulting from addition of one electron into the LUMO level of the molecule. The color of the solution in the thin-layer cell also changed from deep green to yellow. The characteristic intramolecular charge-transfer band appeared at 661 nm was almost disappeared because of the newly formed electron-rich semiquinone center (Fc–$snq^{\bullet -}$). The bands at 281 and 341 nm decreased in intensity and new bands at 384 and 640 nm appeared at low intensity. Finally, the spectrum of the reduced species exhibited a characteristic profile for the semiquinone radical anion (Fc–$snq^{\bullet -}$), which was consistent with previously described ferrocene–benzoquinone systems (Fig. 3a).[17a] The original green color and the spectrum of **10e** could be recovered upon re-oxidation during the spectroelectrochemical measurements. The controlled potential coulometric (CPC) study indicated that the number of electrons transferred for the forward and reverse electrochemical reactions of the complex was one for both the reduction and re-oxidation processes, based on the Fc–nq/Fc–$snq^{\bullet -}$ couple. Thus, semiquinone radical anion (Fc–$snq^{\bullet -}$) remained chemically stable throughout the experiment. The first reduction process was complete within 60 s and followed by a second reduction process. In the spectra of **10e** at the more reducing applied potential (E_{app}=−1.75 V), the band at 428 nm disappeared and the intensity of the band at 342 nm increased (Fig. 3b). After electrolysis was completed within 60 s to afford the doubly reduced forms (Fc–nq^{2-}), different spectral changes were monitored for the next times (the inset in Fig. 3b). Moreover, the second reduction process could not fully be reversed upon the applied potential (E_{app}=−0.10 V). This behavior was probably due to the complexation reaction between the dianion (Fc–nq^{2-}) and neutral (Fc–nq) states as predicted from the cyclic voltammetry or decomposition of doubly reduced species (Fc–nq^{2-}) in the thin-layer cell. Fig. 4 shows the UV–vis spectral changes during the oxidation process based on the Fc^{+}–nq/Fc–nq couple at the applied potential (E_{app}=1.30 V). As was observed for the first reduction process, the intensity of the characteristic intramolecular charge-transfer band (the inset) decreased by removing one electron from the HOMO of the molecule during the oxidation process, thereby forming the mono cationic species (Fc^{+}–nq).

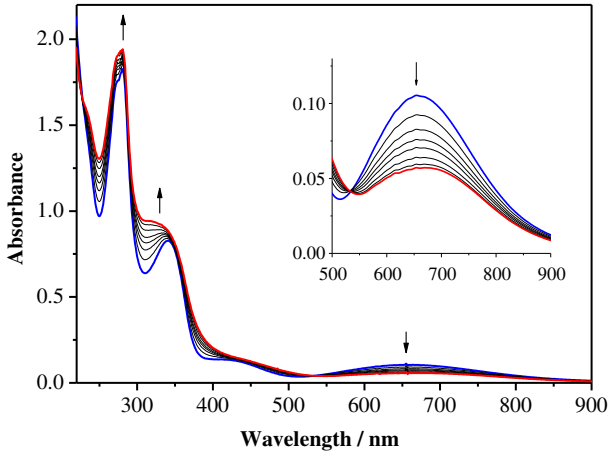


Fig. 4. Time-resolved UV–vis spectral changes of **10e** during the oxidation at E_{app}=1.30 V in CH_3CN solution containing 0.2 M n-Bu_4NClO_4.

All of the spectroscopic changes were fully reversed by re-reduction process at the applied potential (E_{app}=−0.10 V), which indicated a fully reversible oxidation process as predicted from the cyclic voltammetry of **10e**.

2.4. Effect of weak and strong acids on the electrospectroelectrochemistry of the ferrocenyl naphthaquinones

In the presence of acidic additives, electroreduction of quinones is remarkably complex and depends on the effect of acid strength, concentration, and quinone basicity.[15d,f,g,20a,21,22] Addition of acetic

acid (AcOH) into the solution containing the ferrocenyl naphthaquinones did not affect their green color and electronic spectra. This implied that the ferrocenyl naphthaquinones were not protonated in the presence of this weak acid. Fig. 5 exhibits CVs of **10e** before (black line) and after (red line) addition of AcOH.

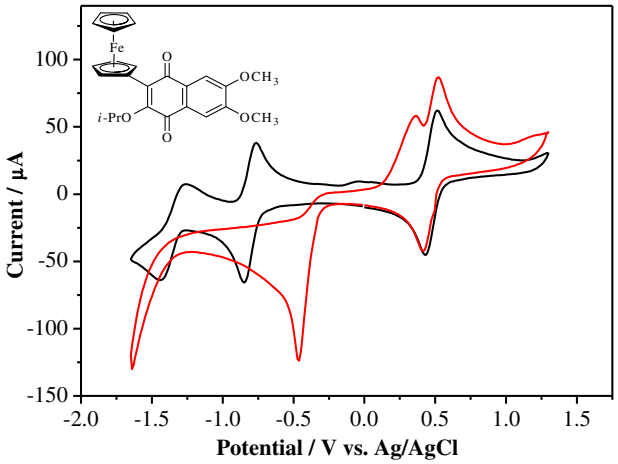


Fig. 5. Cyclic voltammograms of **10e** in CH_3CN solution containing 0.1 M n-Bu_4NClO_4 before addition of AcOH (black line) and after addition of AcOH (40 µL in 4 ml solution) (red line). Scan rates=0.10 V s^{-1}, working electrode: glassy carbon disk electrode (3.0 mm diameter).

The two reduction waves corresponding to Fc–snq$^{\bullet-}$ and Fc–nq^{2-} species in acid-free solution at a scan rate of 0.10 V s^{-1} (black line), are replaced by a large cathodic wave (E_{pc}=−0.46 V) with a higher peak current to form the hydroquinone product (Fc–hnqH_2) by a sequence of two-electron transfer and two-protonation reactions (Fig. 5). The pathway was summarized by green diagonal double arrows in Scheme 8. The anodic wave at more positive potential (E_{pa}=0.36 V) was attributed to the oxidation of the hydroquinone (Fc–hnqH_2) to form the quinone (Fc–nq). Similar behavior was also reported for different hydroquinones lacking the ferrocenyl moiety under weakly acidic conditions.[15f] Fig. 6 exhibits CVs of **10e** before (blue line) and after addition of H_2O (red line), and subsequent addition of trifluoroacetic acid (TFA) (black line).

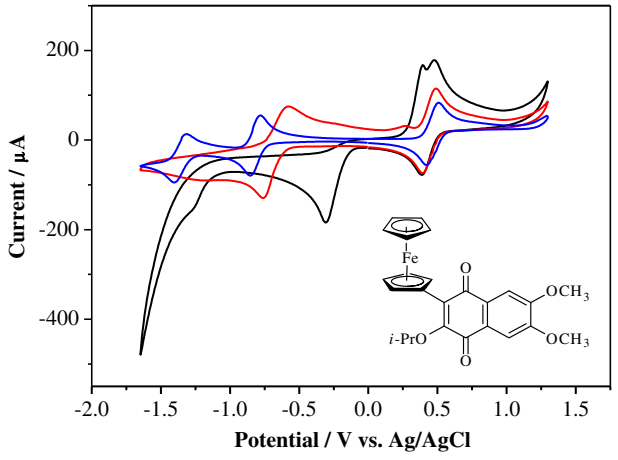


Fig. 6. Cyclic voltammograms of **10e** in CH_3CN solution containing 0.1 M n-Bu_4NClO_4 (blue line), after addition of water (0.1 mL in 4 ml solution) (red line), and after addition of TFA (50 µL in 4 ml solution+0.1 mL water) (black line). Scan rates=0.10 V s^{-1}, working electrode: glassy carbon disk electrode (3.0 mm diameter).

The two reduction waves merged into one by addition of approximately 0.1 mL H_2O (Fig. 6, red line). These results indicated that the reduced species (Fc–snq$^{\bullet-}$ and Fc–nq^{2-}) formed a hydrogen bond with the water in the solvent. In the past, although this phenomenon was often explained by protonation of the quinone dianion species by water,[38] in 1971 Hayano and Fujihira[39] suggested that the positive shift was probably due to hydrogen bonding and several other workers noted that this behavior was not related with protonation.[15d,40] In our case, two well-separated reduction waves, corresponding to the formation of the semiquinone mono- and dianions (Fc–snq$^{\bullet-}$ and Fc–nq^{2-}) shifted positive, with no loss of reversibility by the addition of water. This result was attributed to stabilization by the hydrogen bonding of mono- and dianion reduction products (Fc–snq$^{\bullet-}$ and Fc–nq^{2-}). Eventually, under our experimental conditions, the role of hydrogen bonding could be clearly distinguished from protonation as described by Gupta and Linschitz.[15d] Similarly, the hydrogen bonding interactions between water and the one- and two-electron reduced form of vitamin K_1 based on 2-methly-1,4-naphthaquinone in non-aqueous solvent were recently described by Webster et al.[23a] Scheme 8 (by red double arrows) summarizes the electrochemical pathways for the ferrocenyl naphthaquinones in CH_3CN containing a large amount of water. The CV obtained by subsequent addition of 20 µL TFA (black line in Fig. 6) was similar to that observed for the addition of AcOH. Therefore, the reduced species stabilized by the effect of the hydrogen bonding of water molecules were protonated by the addition of TFA to form the hydroquinone as the final product. The anodic wave appeared at E_{pa}=0.36 V was assigned to the oxidation of the hydroquinone.

The ferrocenyl naphthaquinones in CH_3CN showed different behavior upon the addition of strong acids, such as perchloric acid ($HClO_4$) and trifluoromethanesulfonic acid (TfOH). For example, the color of the solutions, UV–vis spectra and CVs of the ferrocenyl naphthaquinones were considerably changed. These changes clearly indicated a chemical association between proton and quinone groups. Therefore, we conducted electro-spectroelectrochemical studies to understand this proton-coupled electron transfer mechanism of the ferrocenyl naphthaquinones in the presence of strong acids. Addition of $HClO_4$ to solutions of the ferrocenyl naphthaquinones in CH_3CN caused an immediate color change from intense green to deep yellow. In the corresponding UV–vis spectra of Fc–nq, **10e**, the intramolecular charge-transfer band at 695 nm almost disappeared and the bands at 262 and 334 nm (n, $\pi\rightarrow\pi^*$ transitions) increased in intensity (Supplementary data; Fig. S42). These changes were not entirely consistent with the formation of Fc$^+$–nq or Fc$^+$–hnqH_2 species. The lack of Fc$^+$–nq or Fc$^+$–hnqH_2 species in the presence of $HClO_4$ did not thus support disproportionation of the semiquinone (Fc$^+$–snqH$^\bullet$), which was previously proposed for the ferrocenyl-1,4-benzoquinone in strong acids by electro-spectroelectrochemical studies.[17a] The acidic solution containing the semiquinone (Fc$^+$–snqH$^\bullet$) left one green spot on the TLC plate (SiO_2), indicating the stability of the species formed by addition of $HClO_4$. Additionally, the original green color and spectrum (blue dash line) corresponding to **10e** could be achieved again by the addition of SiO_2 as a powder to the solution of **10e** in CH_3CN where SiO_2 probably acted as a base in the presence of strong $HClO_4$ (Supplementary data; Fig. S43). Fig. 7 exhibits CVs of **10e** before (black line) and after (red dash line) addition of $HClO_4$.

The two reduction waves, corresponding to the semiquinone radical anion (Fc–snq$^{\bullet-}$) and the dianion (Fc–nq^{2-}) species in CH_3CN at a scan rate of 0.10 V s^{-1} completely disappeared, and instead, one new cathodic wave at 0.08 V and a corresponding one anodic wave at 0.92 V emerged; yet the position of the oxidation wave of the Fc$^+$–nq/Fc–nq couple did not change. This appearance was partly different than that described by Colbran et al.[17a] Therefore, herein, we proposed a new mechanism in Scheme 9.

According to the proposed mechanism, firstly, the naphthaquinone group was protonated at any oxygen atom to give the ferrocenium semiquinone cation radical (Fc$^+$–snqH$^\bullet$) by addition of $HClO_4$. This provided an increase in the basicity of the

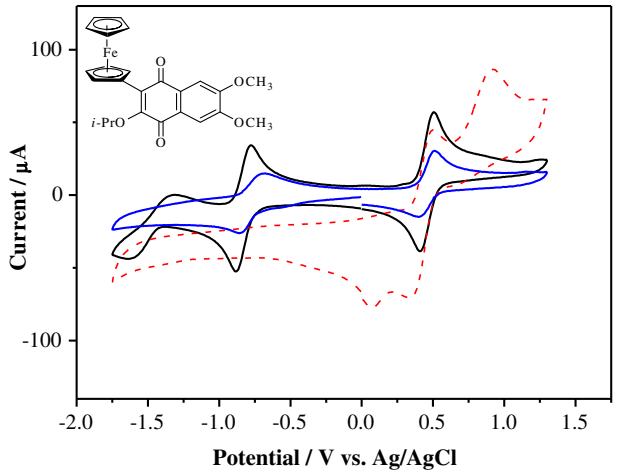


Fig. 7. Cyclic voltammograms of **10e** in CH_3CN solution containing 0.1 M n-Bu_4NClO_4 before addition of $HClO_4$ (black line) and after addition of 40% $HClO_4$ (40 μL in 4 mL solution) (red line), and after addition of excess SiO_2 powder into the solution (blue line). Scan rates=0.10 V s^{-1}, working electrode: glassy carbon disk electrode (3.0 mm diameter).

naphthaquinone by electron delocalization with the donor ferrocene. The proton localized on positions 1 or 4 of the quinone oxygen atom. The cathodic wave observed at 0.08 V is probably based on the hydroquinone (Fc–$hnqH_2$) produced from Fc^+–snqH• by two-electron reduction coupled with one proton. The protonated semiquinone (Fc^+–snqH•) easily reduced than unprotonated counterpart (Fc–snqH•$^-$), thereby the reduction potential of the hydroquinone (Fc^+–$hnqH_2$) in the presence of strong acid appeared at more positive potential (E_{pc}=0.08 V) with respect to that in the presence of weak acid (E_{pc}=−0.46 V). In the first step of anodic scan, Fc–$hnqH_2$ probably oxidized to Fc^+–$hnqH_2$ at 0.51 V by removing one electron from the ferrocene moiety. In the second oxidation step, Fc^+–$hnqH_2$ yielded to Fc^+–nq at 0.92 V by losing two electrons decoupled two protons. The wave occurred at 0.35 V was assigned to the corresponding cathodic wave of Fc^+–$hnqH_2$. The change induced by $HClO_4$ was reversed by addition of a large amount of SiO_2 into the electrochemical cell. The partly original CV of **10e** (blue line) could be obtained except the dianionic wave (Fc–nq^{2-}), probably due to the presence of water to cause hydrogen bonding between the Fc–nq^{2-} species and water (see Fig. 7). Spectral changes for the formation of Fc^+–$hnqH_2$ (the inset) and Fc^+–nq species in thin-layer cell during the applied potentials (E_{app}=0.65 and 1.3 V, respectively) are presented in Fig. 8.

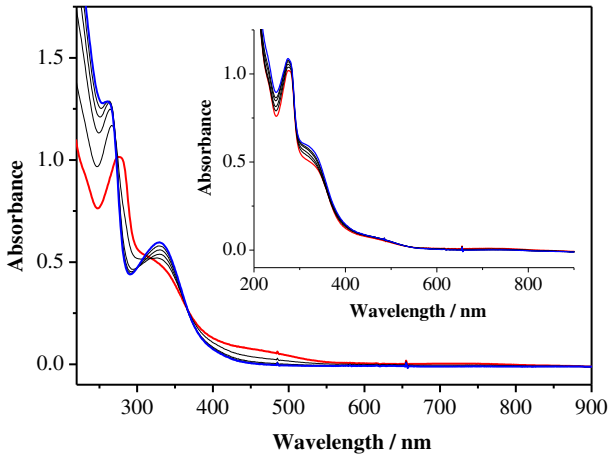
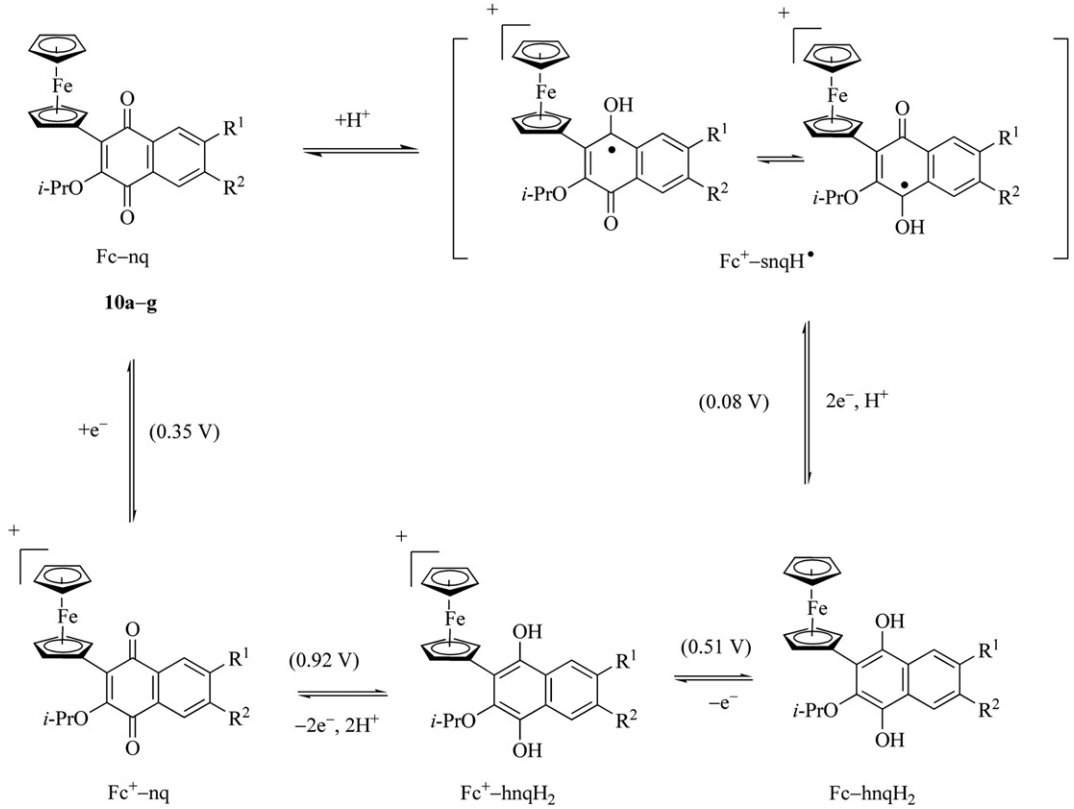


Fig. 8. Time-resolved UV–vis spectral changes of **10e** in the solution of CH_3CN containing excess $HClO_4$ during the oxidation process at E_{app}=1.30 V (supporting electrolyte: 0.2 M n-Bu_4NClO_4). The inset shows the UV–vis spectral changes of **10e** during the oxidation process at E_{app}=0.65 V in the same experimental conditions.



Scheme 9. The electrochemical reduction and oxidation mechanism for the ferrocenyl naphthaquinone derivatives in the solution of CH_3CN after addition of strong acids.

The final spectrum (blue line) corresponding to Fc^{+}–nq species in Fig. 8 was similar to that observed for Fc^{+}–nq species during the oxidation of **10e** (Fig. 4 red line). Addition of TfOH to the solution of the ferrocenyl naphthaquinone **10c** in CH_3CN also caused the color, spectral, and CV changes as in the case of $HClO_4$. One example is given in the Supplementary data (Fig. S44, which represents changes of CVs of **10c** in CH_3CN during repetitive scan after addition of TfOH). The final CV (red line) exhibited general fashion in the strong acid as mentioned above.

3. Conclusions

A highly efficient and practical methodology has been applied for the first time to prepare variously substituted ferrocenyl naphthaquinone derivatives. In this study, molecular complexity of ferrocenyl naphthaquinones has been provided upon the treatment of different aryl lithiums (**7a**–**g**) with 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**). Yet, even by employing 2-lithio-9,9-dibutyl-fluorene (**7h**), 2,7-dilithio-9,9-diethyl-fluorene (**7i**), and 2-bromo-7-lithio-9,9-dibutyl-fluorene (**7j**) oligocyclic ferrocenyl naphthaquinones **10h**–**j** have been easily achieved. Further enlargement of the ferrocenyl naphthaquinone library is still open to investigation through this synthetically flexible methodology. Thus, we are currently working on the synthesis of new derivatives of ferrocenyl naphthaquinones starting from 3,4-bisferrocenyl-3-cyclobutene-1,2-dione[13c,29] and 1,1′-bis{3-(4-isopropoxy-3-cyclobutene-1,2-dioxo)}ferrocene.[29] In this study, the redox chemistry of the ferrocenyl naphthaquinones was examined by electrochemical and in situ spectroelectrochemical techniques in the solution of dichloromethane and acetonitrile. From these studies, it was concluded that the ferrocenyl naphthaquinones **10a**–**k**, **11g**, and **13** showed chemically reversible two reduction processes corresponding to the formation of the semiquinone radical anion ($Fc–snq^{\bullet -}$) and dianion ($Fc–nq^{2-}$) species in non-aqueous solutions, respectively. These complexes displayed chemically reversible one-electron oxidation process based on the ferrocene/ferrocenium (Fc^{+}–nq/Fc–nq) couple. The reduction potentials strongly depend on electron-withdrawing or -donating substituents appended on the naphthaquinone unit. The stability, reversibility and color changes of the reduced [($Fc–snq^{\bullet -}$) and ($Fc–nq^{2-}$)] and oxidized (Fc^{+}–nq) species were clearly demonstrated by thin-layer UV–vis spectroelectrochemisty in non-aqueous solutions. The electrochemistry of the ferrocenyl naphthaquinones was remarkably complex and depended on the acid strength. The reaction mechanism of ferrocenyl naphthaquinones in the presence of acidic additives proceeded via hydrogen bonding or proton-coupled electron transfer. It was also found that the intramolecular charge-transfer for the ferrocenyl naphthaquinones was sensitive to substituents on the napthaquinone center and structural changes caused a shift in the bands to shorter or longer wavelengths. Finally, one can anticipate that ferrocene-naphthaquinone donor–acceptor redox systems involving the range of accessible oxidation states may facilitate a progress in the application of redox-based processes such as the pH-controlled electrochemical switching from the donor centered to the acceptor centered redox chemistry. Additionally, the ferrocenyl naphthaquinones with multiple redox-active centers and possessing low energy charge-transfer transitions may find application in molecular electronics.

4. Experimental

4.1. General considerations

All reagents were used as purchased from commercial suppliers without further purification unless otherwise indicated. Diethyl ether and THF were freshly distilled from sodium/benzophenone ketyl. Acetonitrile (CH_3CN) was distilled over P_2O_5 under vacuum while dichloromethane (CH_2Cl_2) was treated three times with H_2SO_4 and distilled over P_2O_5 and CaH_2 prior to use. Tetra-*n*-butylammonium perchlorate used as supporting electrolyte (*n*-Bu_4NClO_4, Fluka Chemical Co.) was recrystallized from ethyl alcohol and dried in a vacuum oven at 40 °C for at least 1 week prior to use. Solvents for column chromatography, ethyl acetate, and hexane were distilled in a rotary evaporator. Chromatographic separations were performed with Merck Silica 60 (200–400 or 70–230 mesh). TLC was performed with Merck TLC Silicagel60 F_{254} plates, detection was under UV light at 254 nm.

The following compounds were prepared according to known literature methods: 3-isopropoxy-4-ferrocenyl-3-cyclobutene-1,2-dione (**6**),[13c,29] 2-bromo-9,9-dibutyl-fluorene,[41] 2,7-dibromo-9,9-diethyl-fluorene,[42] 2,7-dibromo-9,9-dibutyl-fluorene,[43] and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dibutylfluorene (**12**).[43]

4.1.1. Measurements. NMR spectra were recorded with a Bruker AM 250 (250 MHz for ^1H and 62.9 MHz for ^{13}C NMR), a Bruker Spectrospin Avance DPX400 Ultrashield (400 MHz for ^1H and 100.59 MHz for ^{13}C NMR) and Varian Inova 500 (500 MHz for ^1H and 125 MHz for ^{13}C NMR) instruments. Chemical shifts δ were given in parts per million relative to residual peaks of deuterated solvents and coupling constants, *J*, were given in hertz. The following abbreviations are used to describe spin multiplicities in ^1H NMR spectra: s=singlet; br s=broad singlet; d=doublet; t=triplet; q=quartet; dd=doublet of doublets; m=multiplets. Multiplicities in ^{13}C NMR spectra were determined by DEPT (Distortionless Enhancement by Polarization Transfer): +=primary or tertiary (positive DEPT signal), −=secondary (negative DEPT Signal), C_{quat}=quaternary carbon atoms or APT (Attached Proton Test) measurements. IR spectra were recorded on a NICOLET 6700 FT IR spectrometer. Low resolution mass spectra (API-ES, 70 eV, and APCI) were obtained on a Agilent 1100 LC–MS instrument equipped with a diode array UV-visible range detector and Thermo LCQ Deca Ion Trap Mass Specrometer (Thermo Finnigan). High resolution mass spectra (HRMS) were obtained on a Waters Synapt Q-TOF-MS spectrometer. Elemental analysis was carried out by the Elementar Micro Vario CHNS Elemental Analyzer instrument in Tübitak Ankara Testing and Analysis Laboratory (ATAL). UV-visible spectra were recorded on Agillent Model 8453 diode array spectrophotometer. Cyclic voltammograms (CV) were carried out using CV measurements with Princeton Applied Research Model 2263 potentiostat controlled by an external PC. A three electrode system [BAS model (Bioanalytical System Inc.) solid cell stand] was used for CV measurements in CH_2Cl_2 and CH_3CN and it consisted of platinum (1.6 mm diameter) and glassy carbon (3.0 mm diameter) disc electrodes as working electrode, a platinum wire counter electrode, and a Ag/AgCl (3 M NaCl) reference electrode. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^{+}) was used as an internal standard but all potentials in the paper are referenced to the Ag/AgCl (3 M NaCl) reference electrode. Solutions containing the ferrocenyl naphthaquinone derivatives were deoxygenated by a stream of high purity nitrogen for at least 5 min before running the experiment and the solution was protected from air by a blanket of nitrogen during the experiment. Controlled potential electrolysis (CPE) was performed with Princeton Applied Research Model 2263 potentiostat/Galvanostat. An BAS model electrolysis cell with a fritted glass to separate the cathodic and anodic portions of the cell was used for bulk electrolysis. The sample and solvent were placed into the electrolysis cell under nitrogen. The platinum electrode was polished on alumina (<10 μM) slurries on BAS felt-pad. This was followed by rinsing with Millipore water and then ethanol. UV-visible spectroelectrochemical experiments were

performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode.[44] Potentials were applied and monitored with a Princeton Applied Research Model 2263 potentiostat. Time-resolved UV-visible spectra were recorded on Agillent Model 8453 diode array spectrophotometer.

4.2. General procedure for the synthesis of ferrocenyl naphthaquinones (10b–k)

To a solution of arylbromide (1.0 equiv) in THF at −78 °C under nitrogen, *n*-BuLi (1.1, 1.35 or 2.4 equiv of a 1.6 M of hexane solution) was added via syringe over 15 min. The resulting mixture was stirred at −78 °C for 1 h and then transferred via cannula to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.1 or 2.2 equiv) in THF at −78 °C under the nitrogen atmosphere. After stirring 3 h at −78 °C, the reaction mixture was quenched with 10% NH_4Cl (30 mL) solution at −78 °C and then allowed to warm to rt. The mixture diluted with ether (100 mL) and the organic layer was separated. The aqueous layer was extracted with ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and filtered. The solution concentrated under reduced pressure and the remaining crude material was dissolved in *p*-xylene. The resulting solution was heated at reflux open to the air in a preheated oil bath (165 °C) for 4 h. After removal of the *p*-xylene under reduced pressure, the residue was dissolved in ether (50 mL) and silica gel (3.00 g) was added into the solution. The solution was concentrated under reduced pressure and the green solid residue was subjected to purification by chromatography on silica gel.

*4.2.1. 2-Ferrocenyl-4-hydroxy-3-isopropoxy-4-phenylcyclobut-2-en-1-one (**8a**).* To a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 2.27 g, 7.00 mmol, 1.0 equiv) in THF (40 mL) at −78 °C under a nitrogen atmosphere, PhLi (5.80 mL of a 1.8 M of dibutylether solution, 10.5 mmol, 1.5 equiv) was added. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% NH_4Cl (30 mL) solution at −78 °C and then allowed to warm to rt. The mixture diluted with ether (100 mL) and the organic layer was separated. The aqueous layer was extracted with ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and filtered. The solution concentrated under reduced pressure and the remaining reddish-brown oil residue was subjected to purification by chromatography on silica gel using 2:1 hexane/ethyl acetate as eluent to yield **8a** (1.67 g, 59%, brown solid). Mp 121 °C, R_f=0.23 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.13 (d, J=5.9 Hz, 3H, *i*-PrO [CH_3]), 1.45 (d, J=5.9 Hz, 3H, *i*-PrO [CH_3]), 3.46 (s, 1H, OH), 4.18 (s, 5H, Fc), 4.27 (s, 2H, Fc), 4.71 (s, 2H, Fc), 4.71–4.80 (m, 1H, *i*-PrO [CH]), 7.33–7.42 (m, 3H, Ar), 7.54–7.57 (m, 2H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.51 (CH_3, *i*-PrO), 22.92 (CH_3, *i*-PrO), 67.67 (CH), 68.82 (CH), 69.38 (5×CH, Fc), 70.47 (CH), 78.42 (C_{quat}), 93.60 (C_{quat}), 125.58 (CH, Ph), 126.90 (C_{quat}), 128.05 (C_{quat}), 128.57 (CH, Ph), 137.27 (C_{quat}), 177.65 (C_{quat}), 187.35 (C_{quat}, C=O); IR (ATR): ν=3234 (s), 3066 (w), 2979 (w), 1738 (s), 1619 (vs), 1471 (s), 1450 (m), 1344 (s), 1326 (s), 1203 (m), 1133 (w), 1093 (s), 1039 (s), 1001 (w), 987 (w), 842 (w); MS (APCI) m/z (%): 403 (19) [M^++1], 385 (100), 343 (60); HRMS [TOF MS ES$^+$]: m/z [M]$^+$ calcd. For $C_{23}H_{22}FeO_3$ 402.0918, found 402.0907 (−2.7 ppm).

*4.2.2. 2-Ferrocenyl-3-isopropoxynaphthalene-1,4-dione (**10a**).* 2-Ferrocenyl-4-hydroxy-3-isopropoxy-4-phenylcyclobut-2-en-1-one (**8a**, 1.00 g, 2.49 mmol) was dissolved in *p*-xylene (20 mL). The resulting solution was heated at reflux under a nitrogen atmosphere in a preheated oil bath (165 °C) for 3 h. After removal of the *p*-xylene in a rotary evaporator, the residue was dissolved in ether (50 mL) and silica gel (3.00 g) was added into the solution. The solution again was concentrated under reduced pressure and the green solid residue was subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10a** (0.51 g, 51%, green solid).

Without isolation of **8a**: To a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.00 g, 3.08 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under a nitrogen atmosphere, PhLi (2.57 mL of a 1.8 M of dibutylether solution, 4.62 mmol, 1.5 equiv) was added. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% NH_4Cl (30 mL) solution at −78 °C and then allowed to warm to rt. The mixture was diluted with ether (100 mL) and the organic layer was separated. The aqueous layer was extracted with ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and filtered. The solution concentrated under reduced pressure and the remaining crude material was dissolved in *p*-xylene (30 mL). The resulting solution was heated at reflux open to the air in a preheated oil bath (165 °C) for 4 h. After removal of the *p*-xylene under reduced pressure, the residue was dissolved in ether (50 mL) and silica gel (3.00 g) was added into the solution. The solution again was concentrated under reduced pressure and the green solid residue was subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10a** (0.56 g, 45%, green solid). Mp 107–109 °C, R_f=0.81 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.29 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.12 (s, 5H, Fc), 4.52 (s, 2H, Fc), 4.84–4.94 (m, 1H, *i*-PrO [CH]), 5.20 (s, 2H, Fc), 7.66–7.75 (m, 2H, Ar), 8.05–8.13 (m, 2H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 22.84 (2×CH_3, *i*-PrO), 70.04 (5×CH, Fc), 70.35 (2×CH, Fc), 72.84 (2×CH, Fc), 74.53 (C_{quat}, Fc), 76.27 (CH, *i*-PrO), 125.78 (CH, Ar), 126.51 (CH, Ar), 131.58 (C_{quat}), 132.89 (C_{quat}), 133.17 (CH, Ar), 133.46 (CH, Ar), 136.27 (C_{quat}), 154.61 (C_{quat}), 181.08 (C_{quat}, C=O), 184.67 (C_{quat}, C=O); IR (ATR): ν=2975 (w), 2926 (w), 1651 (vs), 1591 (s), 1552 (s), 1439 (m), 1384 (m), 1341 (s), 1292 (s), 1198 (s), 1099 (s), 998 (vs), 804 (vs); MS (70 eV, API-ES) m/z (%): 401 (72) [M^++1], 400 (100) [M^+], 359 (33), 358 (40), 271 (17), 230 (29), 200 (14), 149 (5); HRMS [TOF MS ES$^+$]: m/z [M]$^+$ calcd. For $C_{23}H_{20}FeO_3$ 400.0762, found 400.0761 (−0.2 ppm).

*4.2.3. 6-Bromo-3-ferrocenyl-2-isopropoxynaphthalene-1,4-dione (**10b**).* According to general procedure, to a solution of 1,4-dibromobenzene (0.66 g, 2.80 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under nitrogen, *n*-BuLi (1.92 mL of a 1.6 M of hexane solution, 3.08 mmol, 1.1 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.00 g, 3.08 mmol, 1.1 equiv) in THF (10 mL) at −78 °C under nitrogen atmosphere. After stirring 3 h at −78 °C and work-up, the crude alcohol **8b** was heated at reflux in *p*-xylene (30 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10b** (0.66 g, 49%, green solid). Mp 150–152 °C, R_f=0.70 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.29 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.13 (s, 5H, Fc), 4.56 (s, 2H, Fc), 4.86–4.95 (m, 1H, *i*-PrO [CH]), 5.20 (s, 2H, Fc), 7.79–7.93 (m, 2H, Ar), 8.23 (s, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.85 (2×CH_3, *i*-PrO), 70.12 (5×CH, Fc), 70.54 (2×CH, Fc), 72.87 (2×CH, Fc), 74.34 (C_{quat}, Fc), 76.49 (CH, *i*-PrO), 127.47 (CH, Ar), 128.90 (C_{quat}), 129.61 (CH, Ar), 130.20 (C_{quat}), 133.96 (C_{quat}), 136.13 (CH, Ar), 136.33 (C_{quat}), 154.57 (C_{quat}), 180.17 (C_{quat}; C=O), 183.37 (C_{quat}; C=O); IR (ATR): ν=2961 (w), 2924 (w), 1725 (w), 1645 (vs), 1580 (m), 1542 (s), 1461 (w), 1382 (w), 1339 (m), 1290 (vs), 1248 (s), 1211 (s), 1196 (s), 1102 (s), 1090 (m), 1003 (vs), 908 (m), 921 (m), 810 (s), 802 (s), 744 (vs); MS (70 eV, API-ES) m/z (%): 481 (55) [M^++1], 480 (100) [M^+], 479 (47), 478 (91), 476 (10), 459(21), 458 (11), 457 (14), 436 (9), 413 (5); HRMS [TOF MS ES$^+$]: m/z [M]$^+$ calcd. For $C_{23}H_{19}BrFeO_3$ 477.9867, found 477.9877 (2.1 ppm).

*4.2.4. 3-Ferrocenyl-6-(trifluoromethyl)-2-isopropoxynaphthalene-1,4-dione (**10c**).* According to general procedure, to a solution of 4-

bromobenzotrifluoride (0.63 g, 2.80 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under nitrogen, *n*-BuLi (2.40 mL of a 1.6 M of hexane solution, 3.78 mmol, 1.35 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.00 g, 3.08 mmol, 1.1 equiv) in THF (20 mL) at −78 °C under a nitrogen atmosphere. After stirring 3 h at −78 °C and work-up, the crude alcohol **8c** was heated at reflux in *p*-xylene (45 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10c** (0.68 g, 52%, green solid). Mp 152–153 °C, R_f=0.78 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.30 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.14 (s, 5H, Fc), 4.58 (s, 2H, Fc), 4.93 (p, J=6.1 Hz, 1H, *i*-PrO [CH]), 5.22 (s, 2H, Fc), 7.92–8.21 (AB system, δ_A=8.20, δ_B=7.94, J_{AB}=7.9 Hz, 2H, Ar), 8.39 (s, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ=22.82 (2×CH_3, *i*-PrO), 70.93 (5×CH, Fc), 71.54 (2×CH, Fc), 73.61 (2×CH, Fc), 74.80 (C_{quat}, Fc), 76.51 (CH, *i*-PrO), 122.97 (q, CF_3, $^1J_{FC}$=273 Hz), 123.49 (C_{quat}), 126.17 (C_{quat}), 129.27 (C_{quat}), 133.09 (CH, Ar), 133.66 (CH, Ar), 134.91 (q, C_{quat}, $^2J_{FC}$=33 Hz), 137.52 (CH, Ar), 154.33 (C_{quat}), 179.71 (C_{quat}; C=O), 183.01 (C_{quat}; C=O); IR (ATR): ν=3086 (w), 2980 (w), 1652 (vs), 1551 (m), 1440 (w), 1324 (m), 1286 (s), 1254 (m), 1205 (m), 1165 (m), 1126 (s), 1101 (s), 1064 (m), 1005 (s), 898 (w), 814 (m), 748 (m), 710 (m); MS (APCI) *m*/*z* (%): 469 (100) [M^++1], 426 (77), 419 (24); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{24}H_{19}F_3FeO_3$ 468.0636, found 468.0638 (0.4 ppm).

*4.2.5. 3-Ferrocenyl-2-isopropoxy-6-methoxynaphthalene-1,4-dione (**10d**).* According to general procedure, to a solution of 4-bromoanisole (0.30 g, 1.60 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under nitrogen, *n*-BuLi (1.35 mL of a 1.6 M of hexane solution, 2.16 mmol, 1.35 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 0.57 g, 1.76 mmol, 1.1 equiv) in THF (10 mL) at −78 °C under a nitrogen atmosphere. After stirring 3 h at −78 °C and work-up, the crude alcohol **8d** was heated at reflux in *p*-xylene (50 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10d** (0.36 g, 53%, green solid). Mp 133–135 °C, R_f=0.74 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.28 (d, J=6.0 Hz, 6H, *i*-PrO), 3.97 (s, 3H, OCH_3), 4.12 (s, 5H, Fc), 4.50 (s, 2H, Fc), 4.90 (p, J=6.0 Hz, 1H, *i*-PrO), 5.17 (s, 2H, Fc), 7.16 (d, J=8.5 Hz, 1H, Ph), 7.57 (s, 1H, Ph), 8.00 (d, J=8.7 Hz, 1H, Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ=22.85 (+, *i*-PrO), 55.90 (+, OCH_3), 69.95 (+, Fc), 70.08 (+, Fc), 72.63 (+, Fc), 74.72 ($C_{quar.}$, Fc), 76.38 (+,*i*-PrO), 109.96 (+, Ph), 119.80 (+, Ph), 125.05 ($C_{quar.}$), 128.25 (+, Ph), 135.01 ($C_{quar.}$), 135.45 ($C_{quar.}$), 154.96 ($C_{quar.}$), 164.05 ($C_{quar.}$), 180.24 (C=O), 184.61 (C=O); IR (ATR): ν=2970, 2929, 1652, 1600, 1582, 1553, 1496, 1464, 1441, 1349, 1332, 1234, 1207, 1176, 1098, 1000, 903, 881, 806 cm^{-1}; MS (70 eV, EI), *m*/*z* (%): 431 (12) [M^+], 430 (42), 388 (100), 295 (18), 281 (23), 207 (87), 121 (29), 73 (68). $C_{24}H_{22}FeO_4$ (430.29): calcd. C 66.99, H 5.15; found C 66.83, H 5.13.

*4.2.6. 2-Ferrocenyl-3-isopropoxy-6,7-dimethoxynaphthalene-1,4-dione (**9e**).* According to general procedure, to a solution of 4-bromoveratrole (0.61 g, 2.80 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under nitrogen, *n*-BuLi (2.36 mL of a 1.6 M of hexane solution, 3.78 mmol, 1.35 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.00 g, 3.08 mmol, 1.1 equiv) in THF (10 mL) at −78 °C under a nitrogen atmosphere. After stirring 3 h at −78 °C and work-up, the crude alcohol **8e** was heated at reflux in *p*-xylene (30 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10e** (0.62 g, 48%, green solid). Mp 151–153 °C, R_f=0.44 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.02 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 4.15 (s, 5H, Fc), 4.53 (s, 2H, Fc), 4.79–4.84 (m, 1H, *i*-PrO [CH]), 5.20 (s, 2H, Fc), 7.49 (s, 1H, Ar), 7.54 (s, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.80 (2×CH_3, *i*-PrO), 56.38 (2×OCH_3), 69.93 (5×CH, Fc), 70.09 (2×CH, Fc), 72.68 (2×CH, Fc), 74.79 (C_{quat}, Fc), 76.19 (CH, *i*-PrO), 107.3 (CH, Ar), 108.2 (CH, Ar), 125.9 (C_{quat}), 127.5 (C_{quat}), 135.30 (C_{quat}), 153.0 (C_{quat}), 153.3 (C_{quat}), 154.4 (C_{quat}), 180.4 (C_{quat}; C=O), 184.1 (C_{quat}; C=O); IR (ATR): ν=2962 (w), 2936 (w), 1656 (s), 1648 (s), 1583 (s), 1567 (s), 1512 (s), 1449 (m), 1464 (s), 1370 (m), 1316 (s), 1302 (s), 1259 (m), 1242 (m), 1192 (m), 1157 (m), 1096 (s), 1057 (w), 1014 (w), 982 (w), 884 (w), 745 (s); MS (APCI) *m*/*z* (%): 461 (100) [M^++1], 431 (20), 418 (45), 411 (14), 371 (10), 279 (46), 117 (43), 97 (22); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{25}H_{24}FeO_5$ 460.0973, found 460.0988 (3.3 ppm).

*4.2.7. 6-Ferrocenyl-7-isopropoxynaphtho[2,3-d][1,3]dioxole-5,8-dione (**10f**).* According to general procedure, to a solution of 4-bromo-1,2-(methylenedioxy)benzene (1.10 g, 5.50 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under nitrogen, *n*-BuLi (4.60 mL of a 1.6 M of hexane solution, 7.38 mmol, 1.35 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.96 g, 6.05 mmol, 1.1 equiv) in THF (20 mL) at −78 °C under a nitrogen atmosphere. After stirring 2.5 h at −78 °C and work-up, the crude alcohol **8f** was heated at reflux in *p*-xylene (45 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10f** (1.08 g, 44%, green solid). Mp 152–153 °C, R_f=0.57 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.12 (s, 5H, Fc), 4.51 (s, 2H, Fc), 4.79–4.84 (m, 1H, *i*-PrO [CH]), 5.16 (s, 2H, Fc), 6.12 (s, 2H, CH_2), 7.44 (s, 1H, Ar), 7.50 (s, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.80 (2×CH_3, *i*-PrO), 69.99 (5×CH, Fc), 70.21 (2×CH, Fc), 72.72 (2×CH, Fc), 74.70 (C_{quat}, Fc), 76.25 (CH, *i*-PrO), 102.44 (CH_2), 105.28 (CH, Ar), 106.19 (CH, Ar), 128.25 (C_{quat}), 129.93 (C_{quat}), 135.34 (C_{quat}), 151.82 (C_{quat}), 152.12 (C_{quat}), 154.15 (C_{quat}), 180.0 (C_{quat}; C=O), 183.59 (C_{quat}; C=O); IR (ATR): ν=2961(w), 2929 (w), 1639 (s), 1596 (s), 1569 (s), 1508 (m), 1477 (s), 1449 (m), 1403 (m), 1380 (m), 1301 (s), 1254 (s), 1214 (w), 1141 (m), 1102 (m), 1061 (m), 1027 (s), 997 (s), 923 (m), 882 (m), 809 (s), 741 (s); MS (70 eV, ES) *m*/*z* (%): 445 (42) [M^++1], 444 (100) [M^+], 424 (29), 413 (67), 392 (23), 301 (20), 283 (39), 236 (36), 214 (19); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{24}H_{20}FeO_5$ 444.0660, found 444.0657 (−0.7 ppm).

*4.2.8. 7-Ferrocenyl-2,3-dihydro-8-isopropoxynaphtho[2,3-b][1,4]dioxine-6,9-dione (**10g**) and 9-ferrocenyl-2,3-di-hydro-8-isopropoxynaphtho[2,1-b][1,4]dioxine-7,10-dione (**11g**).* According to general procedure, to a solution of 6-bromo-1,4-benzodioxane (0.60 g, 2.80 mmol, 1.0 equiv) in THF (10 mL) at −78 °C under nitrogen, *n*-BuLi (2.36 mL of a 1.6 M of hexane solution, 3.78 mmol, 1.35 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.00 g, 3.08 mmol, 1.1 equiv) in THF (10 mL) at −78 °C under a nitrogen atmosphere. After stirring 2.5 h at −78 °C and work-up, the crude alcohol **8g** was heated at reflux in *p*-xylene (30 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10g** (0.51 g, 40%, green solid) and **11g** (0.17 g, 13%, green solid). Compound (**10g**): mp 133–135 °C, R_f=0.39 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.27 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.12 (s, 5H, Fc), 4.35 (s, 4H, 2×CH_2), 4.51 (s, 2H, Fc), 4.81–4.85 (m, 1H, *i*-PrO [CH]), 5.19 (s, 2H, Fc), 7.52 (s,

1H, Ar), 7.56 (s, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.79 (2×CH_3, *i*-PrO), 64.53 (CH_2), 64.59 (CH_2), 70.14 (5×CH, Fc), 70.30 (2×CH, Fc), 72.90 (2×CH, Fc), 74.98 (C_{quat}, Fc), 76.15 (CH, *i*-PrO), 115.13 (CH, Ar), 115.95 (CH, Ar), 126.43 (C_{quat}), 127.99 (C_{quat}), 135.93 (C_{quat}), 147.82 (C_{quat}), 148.14 (C_{quat}), 154.69 (C_{quat}), 180.15 (C_{quat}; C=O), 183.70 (C_{quat}; C=O); IR (ATR):ν=976 (w), 1650 (s), 1595 (s), 1539 (s), 1496 (m), 1438 (m), 1382 (m), 1349 (m), 1317 (s), 1292 (s), 1255 (s), 1190 (w), 1162 (m), 1143 (w), 1102 (m), 1022 (m), 1000 (m), 925 (w), 888 (s), 734 (s); MS (70 eV, API-ES) *m*/*z* (%): 460 (28) [M^++2], 459 (93) [M^++1], 458 (100) [M^+], 457 (88), 417 (21), 416 (16), 314 (46), 286 (32), 258 (22), 230 (77), 219 (21), 163 (29), 149 (14); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{25}H_{22}FeO_5$ 458.0817, found 458.0809 (−1.7 ppm).

Compound (**11g**): mp 171–172 °C, R_f=0.25 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.27 (d, *J*=6.2 Hz, 6H, 2×*i*-PrO [CH_3]), 4.15 (s, 5H, Fc), 4.28–4.49 [m, 6H, Fc (2H); 2×CH_2], 4.80–4.85 (m, 1H, *i*-PrO [CH]), 5.21 (s, 2H, Fc), 7.11 (d, *J*=8.4 Hz, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.76 (2×CH_3, *i*-PrO), 63.15 (CH_2), 63.53 (CH_2), 68.96 (5×CH, Fc), 69.16 (2×CH, Fc), 71.61 (2×CH, Fc), 73.71 (C_{quat}, Fc), 74.74 (CH, *i*-PrO), 119.30 (CH, Ar), 120.06 (CH, Ar), 121.13 (C_{quat}), 125.28 (C_{quat}), 136.25 (C_{quat}), 142.58 (C_{quat}), 148.07 (C_{quat}), 151.97 (C_{quat}), 179.35 (C_{quat}; C=O), 183.44 (C_{quat}; C=O); IR (ATR): ν=2974 (w), 2929 (w), 1655 (s), 1597 (w), 1578 (s), 1482 (m), 1455 (m), 1429 (m), 1375 (w), 1342 (w), 1279 (s), 1211 (s), 1174 (m), 1140 (w), 1104 (s), 1092 (s), 1002 (s), 972 (w), 957 (m), 901 (s), 841 (m), 806 (s), 765 (s); MS (70 eV, API-ES) *m*/*z* (%): 460 (26) [M^++2], 459 (100) [M^++1], 458 (55) [M^+], 457 (25), 416 (23), 258 (63); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{25}H_{22}FeO_5$ 458.0817, found 458.0820 (0.7 ppm).

*4.2.9. 11,11-Dibutyl-7-ferrocenyl-8-isopropoxy-11H-benzo[b]fluorene-6,9-dione(**10h**).* According to general procedure, to a solution of 2-bromo-9,9-dibutyl-fluorene (2.00 g, 5.6 mmol, 1.0 equiv) in THF (30 mL) at −78 °C under nitrogen, *n*-BuLi (4.84 mL of a 1.6 M of hexane solution, 7.73 mmol, 1.38 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 2.00 g, 6.17 mmol, 1.1 equiv) in THF (30 mL) at −78 °C under a nitrogen atmosphere. After stirring 2.5 h at −78 °C and work-up, the crude alcohol **8h** was heated at reflux in *p*-xylene (60 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10h** (1.34 g, 40%, green solid). Mp 173–175 °C, R_f=0.79 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.54–0.69 (m, 10H, 2×CH_3, 2×CH_2), 1.04–1.13 (m, 4H, 2×CH_2), 1.32 (d, *J*=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 2.01–2.09 (m, 4H, 2×CH_2), 4.16 (s, 5H, Fc), 4.53 (s, 2H, Fc), 4.88–4.93 (m, 1H, *i*-PrO [CH]), 5.21 (s, 2H, Fc), 7.41–7.43 (m, 3H, Ar), 7.87–7.90 (m, 1H, Ar), 8.03 (s, 1H, Ar), 8.42 (s, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.83 (2×CH_3), 22.96 (2×CH3, *i*-PrO [CH_3]), 22.96 (2×CH_2), 26.00 (2×CH_2), 39.94 (2×CH_2), 55.88 (C_{quat}), 70.05 (5×CH, Fc), 70.23 (2×CH, Fc), 72.84 (2×CH, Fc), 74.83 (C_{quat}, Fc), 76.42 (CH, *i*-PrO), 117.80 (CH, Ar), 120.21 (CH, Ar), 121.28 (CH, Ar), 123.12 (CH, Ar), 127.41 (CH, Ar), 129.06 (CH, Ar), 130.52 (C_{quat}), 132.85 (C_{quat}), 135.92 (C_{quat}), 139.40 (C_{quat}), 146.61 (C_{quat}), 151.72 (C_{quat}), 155.03 (C_{quat}), 156.07 (C_{quat}), 181.40 (C_{quat}; C=O), 185.08 (C_{quat}; C=O); IR (ATR): ν=2957 (w), 2927 (w), 2857 (w), 1654 (s), 1602 (m), 1561 (m), 1448 (w), 1381(w), 1365 (w), 1320 (s), 1300 (s), 1284 (s), 1234 (w), 1244 (w), 1202 (m), 1184 (w), 1166 (w), 1097 (s), 1085 (s), 1054 (w), 1016 (s), 937 (w), 906 (w), 812 (m), 743 (s); MS (APCI) *m*/*z* (%): 601 (100) [M^++1], 559 (40), 551 (12), 494 (10), 393 (6), 305 (5), 281 (6); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{38}H_{40}FeO_3$ 600.2327, found 600.2322 (−0.8 ppm).

*4.2.10. 12,12-Diethyl-7,8-diferrocenyl-2,9-diisopropoxy-12H-dibenzo[b,h]fluorene-1,4,7,10-tetrone (**10i**).* According to general procedure, to a solution of 2,7-dibromo-9,9-diethyl-fluorene (0.41 g, 1.06 mmol, 1.0 equiv) in THF (15 mL) at −78 °C under nitrogen, *n*-BuLi (1.60 mL of a 1.6 M of hexane solution, 2.54 mmol, 2.4 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 0.76 g, 2.33 mmol, 2.2 equiv) in THF (15 mL) at −78 °C under a nitrogen atmosphere. After stirring 2.5 h at −78 °C and work-up, the crude alcohol **8i** was heated at reflux in *p*-xylene (30 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10i** (0.22 g, 24%, green solid). Mp 130–131 °C, R_f=0.67 (hexane/ethyl acetate 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.29 (t, *J*=7.3 Hz, 6H, 2×CH_3), 1.25 (d, *J*=6.2 Hz, 12H, 4×*i*-PrO [CH_3]), 2.13 (q, *J*=7.3 Hz, 4H, 2×CH_2), 4.09 (s, 10H, 2×Fc [5*H*]), 4.49 (s, 4H, 2×Fc [2*H*]), 4.82–4.84 (m, 2H, 2×*i*-PrO [CH]), 5.17 (s, 4H, 2×Fc [2*H*]), 8.01 (s, 2H, Ar), 8.56 (s, 2H, Ar); ^{13}C NMR (100.59 MHz, $CDCl_3$): δ=7.60 (2×CH_3), 21.90 (2×CH_3, *i*-PrO [CH_3]), 31.45 (2×CH_2), 56.90 (C_{quat}), 69.10 (5×CH, Fc), 69.45 (2×CH, Fc), 71.94 (2×CH, Fc), 73.64 (C_{quat}, Fc), 75.42 (CH, *i*-PrO), 118.4 (CH, Ar), 119.47 (CH, Ar), 130.80 (C_{quat}), 132.20 (C_{quat}), 135.47 (C_{quat}), 145.86 (C_{quat}), 153.87 (C_{quat}), 154.93 (C_{quat}), 180.04 (C_{quat}; C=O), 183.34 (C_{quat}; C=O); IR (ATR): ν=2964 (w), 2929 (w), 1758 (w), 1656 (s), 1602 (s), 1548 (s), 1440 (m), 1381 (m), 1290 (s), 1245 (m), 1213 (s), 1190 (m), 1169 (m), 1095 (s), 1084 (s), 1065 (m), 940 (w), 903 (s), 804 (s), 730 (s); MS (APCI) *m*/*z* (%): 867 (100) [M^++1]; HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{51}H_{46}Fe_2O_6$ 866.1993, found 866.2028 (4.0 ppm).

*4.2.11. 2-Bromo-11,11-dibutyl-7-ferrocenyl-8-isopropoxy-11H-benzo[b]fluorene-6,9-dione (**10j**).* According to general procedure, to a solution of 2,7-dibromo-9,9-dibutyl-fluorene (0.73 g, 1.68 mmol, 1.0 equiv) in THF (15 mL) at −78 °C under nitrogen, *n*-BuLi (1.25 mL of a 1.6 M of hexane solution, 2.02 mmol, 1.2 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 0.60 g, 1.85 mmol, 1.1 equiv) in THF (15 mL) at −78 °C under a nitrogen atmosphere. After stirring 2.5 h at −78 °C and work-up, the crude alcohol **8j** was heated at reflux in *p*-xylene (30 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10j** (0.70 g, 61%, green solid). Mp 114–116 °C, R_f=0.78 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.57–0.68 (m, 10H, 2×CH_3, 2×CH_2), 1.06–1.11 (m, 4H, 2×CH_2), 1.32 (d, *J*=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 2.01–2.06 (m, 4H, 2×CH_2), 4.16 (s, 5H, Fc), 4.54 (s, 2H, Fc), 4.89–4.92 (m, 1H, *i*-PrO [CH]), 5.21 (s, 2H, Fc), 7.53–7.76 (m, 3H, Ar), 8.02 (s, 1H, Ar), 8.39 (s, 1H, Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.71 (2×CH_3), 22.90 (2×CH3, *i*-PrO [CH_3]), 22.90 (2×CH_2), 25.97 (2×CH_2), 39.85 (2×CH_2), 56.20 (C_{quat}), 70.21 (5×CH, Fc), 70.44 (2×CH, Fc), 72.98 (2×CH, Fc), 74.89 (C_{quat}, Fc), 76.42 (CH, *i*-PrO), 117.89 (CH, Ar), 120.25 (CH, Ar), 122.53 (CH, Ar), 123.38 (C_{quat}), 126.48 (CH, Ar), 130.74 (CH, Ar), 130.82 (C_{quat}), 132.98 (C_{quat}), 136.04 (C_{quat}), 138.41 (C_{quat}), 145.38 (C_{quat}), 153.83 (C_{quat}), 154.97 (C_{quat}), 155.60 (C_{quat}), 181.20 (C_{quat}; C=O), 184.83 (C_{quat}; C=O) [The CH carbon peak of *i*-PrO-group sits under multiplets of $CDCl_3$]; IR (ATR): ν=2955 (w), 2926 (w), 2857 (w), 1652 (s), 1600 (s), 1549 (m), 1443 (m), 1407 (w), 1313 (vs), 1289 (vs), 1270 (m), 1199 (m), 1165 (m), 1098 (s), 1016 (vs), 898 (m), 819 (s), 730 (s); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{38}H_{39}BrFeO_3$ 678.1432, found 678.1426 (−0.9 ppm).

*4.2.12. 6,6′-Bis(3-ferrocenyl-2-isopropoxynaphthalene-1,4-dione) (**10k**).* According to general procedure, to a solution of 4,4′-dibromobiphenyl (0.48 g, 1.54 mmol, 1.0 equiv) in THF (20 mL) at −78 °C under nitrogen, *n*-BuLi (1.93 mL of a 1.6 M of hexane solution, 3.08 mmol, 2 equiv) was added. The resulting mixture was stirred

at −78 °C for 1 h and then transferred to a solution of 3-ferrocenyl-4-isopropoxy-3-cyclobutene-1,2-dione (**6**, 1.00 g, 3.08 mmol, 2.0 equiv) in THF (20 mL) at −78 °C under a nitrogen atmosphere. After stirring 3 h at −78 °C and work-up, the crude alcohol **8k** was heated at reflux in *p*-xylene (30 mL) for 4 h. The crude product was obtained as described in the general procedure and then subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield **10k** (0.54 g, 44%, green solid). Mp 117–119 °C, R_f=0.56 (hexane/ethyl acetate 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.32 (d, J=6.1 Hz, 6H, 2×*i*-PrO [CH_3]), 4.16 (s, 10H, 2×Fc [5*H*]), 4.57 (s, 4H, 2×Fc [2*H*]), 4.92–4.97 (m, 2H, 2×*i*-PrO [CH]), 5.24 (s, 4H, 2×Fc [2*H*]), 8.02–8.22 (AB system, δ_A=8.20, δ_B=8.04, J_{AB}=7.9 Hz, 2H, Ar), 8.47 (s, 2H, 2×Ar); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.88 (4×CH_3, *i*-PrO), 70.12 (10×CH, Fc), 70.52 (4×CH, Fc), 72.90 (4×CH, Fc), 74.53 (2×C_{quat}, Fc), 76.45 (2×CH, *i*-PrO), 125.28 (2×CH, Ar), 126.82 (2×CH, Ar), 131.25 (2×C_{quat}), 131.56 (2×C_{quat}), 133.48 (2×C_{quat}), 136.60 (2×C_{quat}), 144.13 (2×C_{quat}), 154.84 (2×C_{quat}), 180.51 (2×C_{quat}; C=O), 184.31 (2×C_{quat}; C=O); IR (ATR):ν=2972 (w), 2928 (w), 1758 (w), 1649 (s), 1599 (m), 1576 (m), 1542 (m), 1448 (w), 1383 (m), 1343 (m), 1285 (s), 1268 (s), 1198 (s), 1103 (s), 1087 (s), 1041 (s), 916 (m), 805 (s), 778 (m), 738 (s); MS (APCI) *m*/*z* (%): 799 (100) [M^++1], 757 (12), 619 (10); HRMS [TOF MS ES$^+$]: *m*/*z* [M]$^+$ calcd. For $C_{46}H_{38}Fe_2O_6$ 798.1367, found 798.1396 (3.6 ppm).

4.3. Compound (13)

In a screw-cap Pyrex bottle, to a dioxane solution (5.0 mL) of ferrocenyl naphthaquinone **10j** (0.20 g, 0.29 mol) and 2,7-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dibutylfluorene (**12**, 0.71 mg, 0.13 mmol) were added $PdCl_2$(dppf) (22.71 mg, 0.028 mmol), tetrabutylammonium bromide (TBAB) (26.91 mg, 0.08 mmol), and 2 M Na_2CO_3 (0.5 mL) solution. The mixture was stirred at 100 °C for 19 h in a preheated oil bath. After cooling to rt, the reaction mixture was taken up in diethyl ether (20 mL). The solution was washed with water (2×20 mL), the aqueous phase was extracted with diethyl ether (2×20 mL), and the combined organic phases were dried (NaSO4). After removal of the solvent in a rotatory evaporator, the residue was subjected to purification by chromatography on silica gel (100 g, 3×30 cm, hexane/ethyl acetate 20:1) to yield **13** (0.16 g, 83%, green solid). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.68–0.88 (m, 30H, 6×CH_3, 6×CH_2), 1.10–1.25 (m, 12H, 6×CH_2), 1.34 (d, J=6.1 Hz, 12H, 4×*i*-PrO [CH_3]), 2.11–2.17 (m, 12H, 6×CH_2), 4.18 (s, 10H, Fc), 4.55 (s, 4H, Fc), 4.94 (p, J=6.1 Hz, 2H, 2×*i*-PrO [CH]), 5.23 (s, 4H, Fc), 7.69–7.88 (m, 10H, Ar), 7.97–8.01 (m, 2H, Ar), 8.07 (s, 2H, Ar), 8.46 (s, 2H, Ar); ^{13}C NMR (100.59 MHz, $CDCl_3$): δ=13.74 (2×CH_3), 13.80 (CH_3), 22.96 (2×CH_2, 2×CH_3 *i*-PrO [CH_3]), 23.05 (CH_2), 26.08 (2×CH_2), 26.11 (CH_2), 39.95 (2×CH_2), 40.17 (CH_2), 55.34 (C_{quat}), 56.00 (C_{quat}), 70.38 (5×CH, Fc), 70.56 (2×CH, Fc), 73.12 (2×CH, Fc), 76.43 (CH, *i*-PrO), 77.21 (C_{quat}, Fc), 117.78 (CH, Ar), 120.17 (CH, Ar), 120.43 (CH, Ar), 121.49 (CH, Ar), 121.52 (CH, Ar), 121.55 (CH, Ar), 126.29 (CH, Ar), 126.71 (CH, Ar), 130.41 (C_{quat}), 132.93 (C_{quat}), 135.92 (C_{quat}), 138.55 (C_{quat}), 140.01 (C_{quat}), 140.33 (C_{quat}), 142.43 (C_{quat}), 146.25 (C_{quat}), 151.93 (C_{quat}), 152.54 (C_{quat}), 156.02 (C_{quat}), 156.26 (C_{quat}), 181.32 (C_{quat}; C=O), 185.05 (C_{quat}; C=O); IR (ATR):ν=2956 (m), 2929 (s), 2859 (m), 1655 (vs), 1599 (vs), 1552 (m), 1463 (m), 1380 (w), 1319 (vs), 1292 (vs), 1203 (s), 1166 (m), 1100 (s), 1083 (m), 1017 (vs), 898 (m), 816 (vs), 743 (s); MS (APCI) *m*/*z* (%): 1476 (100) [M^++1], 1434 (18), 1224 (10), 391 (18), 278 (31).

4.4. 2,3-Diisopropoxy-1,4-naphthaquinone (14)

To a solution of 3,4-diisopropoxycyclobut-3-ene-1,2-dione[30b] (1.50 g, 7.57 mmol, 1.0 equiv) in THF (30 mL) at −78 °C under a nitrogen atmosphere, PhLi (6.30 mL of a 1.8 M of dibutylether solution, 11.34 mmol, 1.5 equiv) was added. After stirring 3 h at −78 °C, the reaction mixture was quenched with 10% NH_4Cl (20 mL) solution at −78 °C and then allowed to warm to rt. The mixture diluted with ether (100 mL) and the organic layer was separated. The aqueous layer was extracted with ether (2×50 mL). The combined organic layers were dried over Na_2SO_4 and filtered. The solution concentrated under reduced pressure and the remaining crude material was dissolved in *p*-xylene (30 mL). The resulting solution was heated at reflux open to the air in a preheated oil bath (165 °C) for 4 h and then stirred at rt overnight. After removal of the *p*-xylene under reduced pressure, the residue was dissolved in ether (50 mL) and silica gel (3.00 g) was added into the solution. The solution was concentrated under reduced pressure and the green solid residue was subjected to purification by chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent to yield 2,3-diisopropoxy-1,4-naphthaquinone (0.83 g, 40%, yellow oil). For the spectroscopic data of 2,3-diisopropoxy-1,4-naphthaquinone see Ref. 32.

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Supplementary data

^{1}H and ^{13}C NMR spectra of the ferrocenyl naphthaquinones **10a**–**k**, **11g**, **13**, and 4-hydroxycyclobutenone **8a**. Plot of Reichardt's overall solvation scale against band wavelength for the lowest energy transition of **10e** in a variety of solvents. Cyclic voltammograms of **10a** at different scan rates. UV–vis spectral changes of **10e** in the solution of CH_3CN upon addition of 40% $HClO_4$ and after addition of excess SiO_2 powder. Cyclic voltammograms of **10c** recorded during repeating scans after addition of excess TfOH into the CH_3CN solution. Supplementary data associated with this article can be found in the online version at, doi:10.1016/j.tet.2010.12.057.

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