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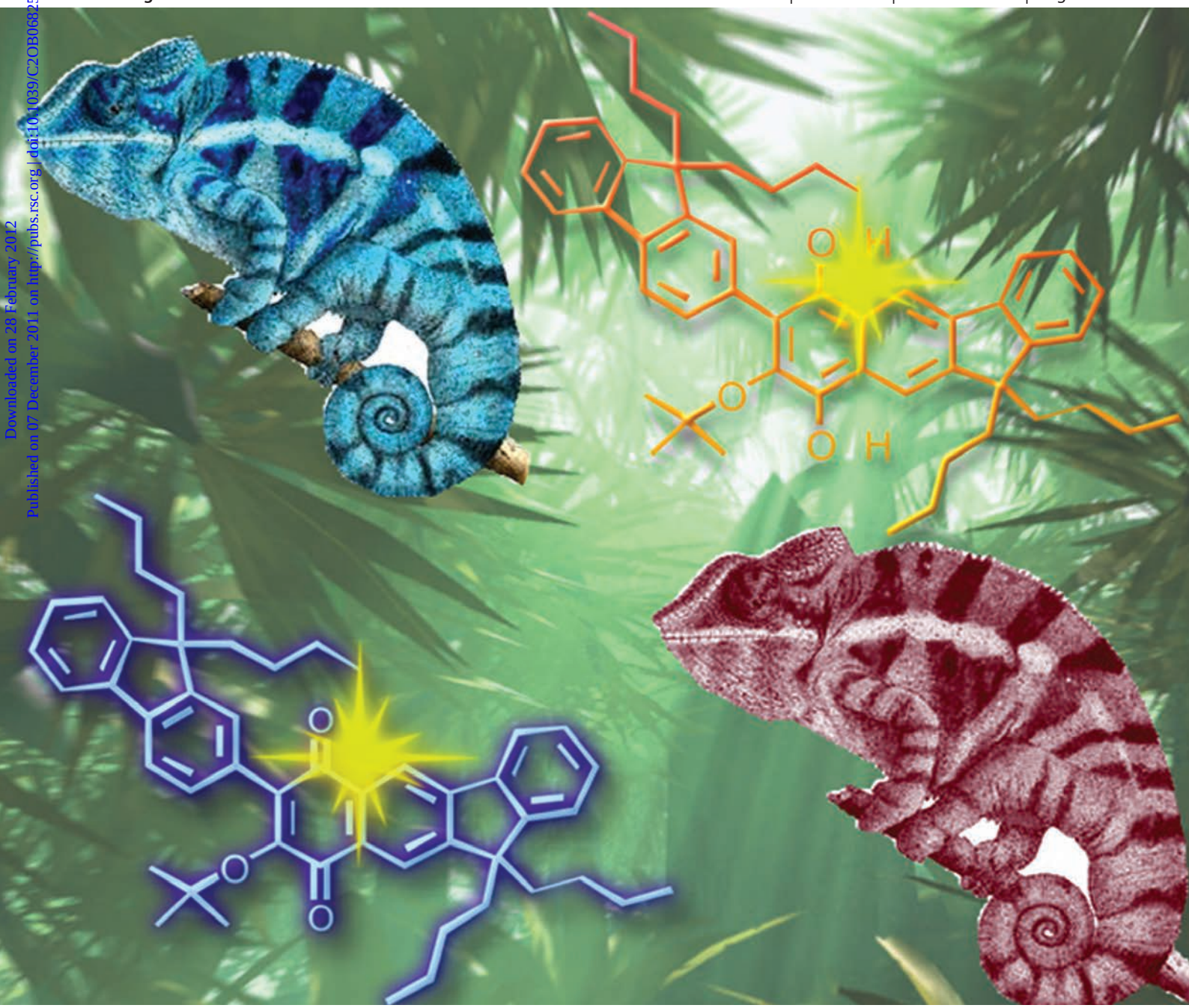

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**PAPER**

# Colour-responsive fluorescent oxy radical sensors†

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A series of fluorene-fused benzoquinones (**Q1–Q5**) were prepared by thermolysis of 4-fluorenyl-4-hydroxycyclobutenones. Red fluorescence observed for **Q2** is switched by reduction to blue fluorescence by formation of the hydroquinone. Reaction with hydrogen peroxide restores the original fluorescence colour. The potential use of compound **Q2** as a reactive oxygen species detector is discussed.

## Introduction

Quinones are one of the most common components of natural and synthetic compounds exhibiting numerous biological properties such as fungitoxic,[1] antibacterial,[2] anti-inflammatory[3] and anticancer activities.[4] Quinone derivatives also play an essential role by carrying electrons in mitochondrial membrane-associated electron-transfer processes.[5] In addition, acenequinones have emerged as key precursors in the area of molecular materials for the synthesis of functionalized acenes that act as semiconducting and emissive layers in organic devices.[6] As an electron acceptor exhibiting well-described reversible electrochemical redox couples, quinones have been combined with electron donors,[7] particularly with ferrocene,[8] to form electron donor–acceptor assemblies for studying electron transfer processes. Moreover, quinones are known to be good fluorescence quenchers and covalently linked to various fluorophores to achieve molecular switches.[9] These fluorescence switches operate by chemically or electrochemically induced redox reactions of quinones, which quench reversibly the singlet state donor fluorescence of fluorophores.[9]

Thus, the preparation of variously substituted quinone derivatives constitutes a significant place in numerous research areas. Several powerful methodologies have been developed to synthesize a wide range of quinone structures.[10] Among them, highly regiospecific thermolysis of 4-alkenyl-, 4-(aryl or heteroaryl)-4-hydroxycyclobutenones as well as 4-alkynyl-4-hyroxycyclobutenones is remarkably important since the method provides easy access to versatile quinones such as aryl, heteroaryl fused and even related polycyclic derivatives.[11] The starting 4-hydroxycyclobutenones are readily available from the corresponding cyclobutenediones by treatment with the respective organolithium reagents.[11] Moreover, accessibility of differently substituted cyclobutendione[12] or even benzocyclobutendione[13] precursors allows enhanced diversity in the structure of quinones. The proposed mechanism for the formation of quinones entails electrocyclic ring opening of 4-hydroxycyclobutenones and subsequent thermally allowed 6π ring closure to afford hydroquinone derivatives after enolization. Initially formed hydroquinones are further oxidized to achieve the desired quinones.[11]

We have recently conceived a simple extension of the methodology for the synthesis of fluorenyl-substituted and fluorene-fused benzoquinone derivatives (Fig. 1) which exhibit rather unique chemically-induced fluorescence switching behaviour. In the quinone state the molecules exhibit a clear red fluorescence glow seen easily by eye, but this is switched to blue upon reduction to the hydroquinone form. We envisaged that such switching behaviour could be put to beneficial use in the detection of reactive oxygen species (ROS) by, in the first instance, turning the probe to the on-state (blue) by reduction of the

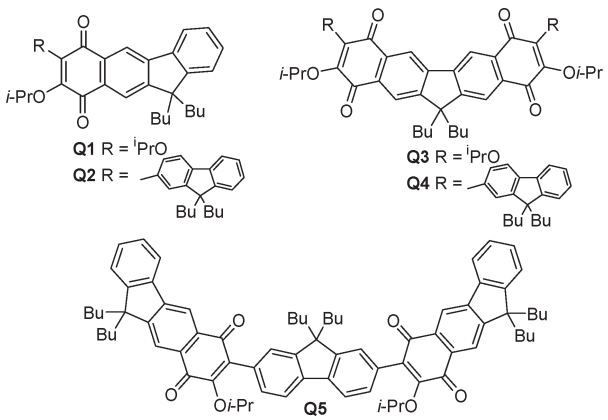


**Fig. 1** Illustrations of quinone derivatives discussed in the text.

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†Electronic supplementary information (ESI) available: Cyclic voltammograms, X-ray structure of **Q2**, computer calculated structures for **Q1** and **Q2**, Absorption spectra, Table of photophysical properties and copies of NMR spectra. CCDC reference number 827083. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob06825g

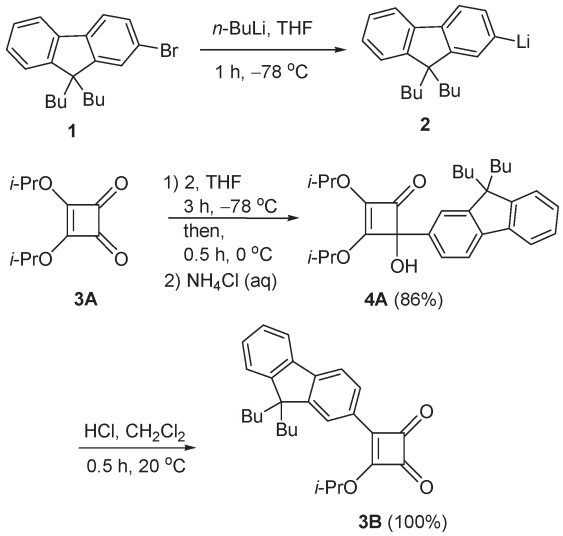
quinone. In principle, such a process could be performed remotely by an electrode, or *in situ* chemically prior to injection at a site in a cell. Reaction of the ROS with the hydroquinone restores the red fluorescence as the quinone resting state is reformed. Such chameleon-like behaviour is very different to conventional oxy radical detectors that are generally fluorescent on/off and often irreversible in their workings.[9a,14] There is considerable growing interest in reversible ROS detectors since they offer the possibility to monitor more precisely the ebb and flow of oxy species. The synthesis and properties of the first prototype reversible colour-shifting fluorescent molecular probes are discussed herein.

## Synthesis

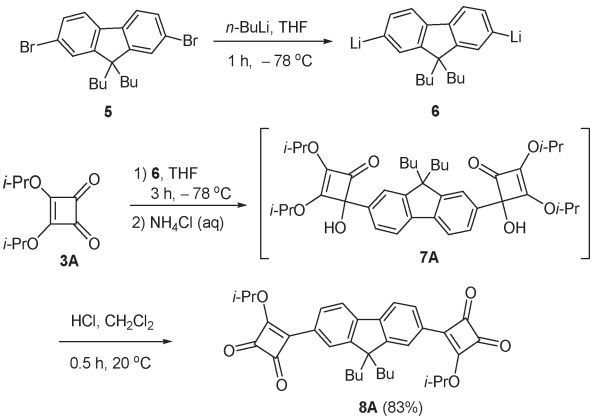
The fluorenyl-substituted cyclobutenedione derivatives (**3B** and **8A**) were initially synthesized starting from diisopropyl squarate **3A**[12b] by following standard literature procedures applied for the synthesis of aryl or heteroaryl-substituted cyclobutenediones.[12] Lithio fluorene **2** was *in situ* prepared by the reaction of a slight excess of *n*-BuLi with the corresponding bromo fluorene **1** in dry THF at −78 °C. This solution when added into the solution of **3A** at −78 °C produced **4A** in 86% yield. Hydrolysis of the intermediate alcohol **4A** in the presence of HCl at room temperature produced fluorenyl-substituted cyclobutenedione **3B** in quantitative yield (Scheme 1).

Similarly, the reaction of 2.2 equiv. of diisopropyl squarate **3A** with 1.0 equiv. of 2,7-dilithio-9,9-dibutyl-fluorene (**6**) at −78 °C furnished a mixture containing intermediate alcohols **7A** after an ammonium chloride quench at −78 °C. The compound **7A** was not isolated from the mixture and was directly hydrolyzed by addition of HCl into the $CH_2Cl_2$ solution of the crude mixture to yield the fluorene-bridged cyclobutenedione **8A** in 83% yield (Scheme 2).

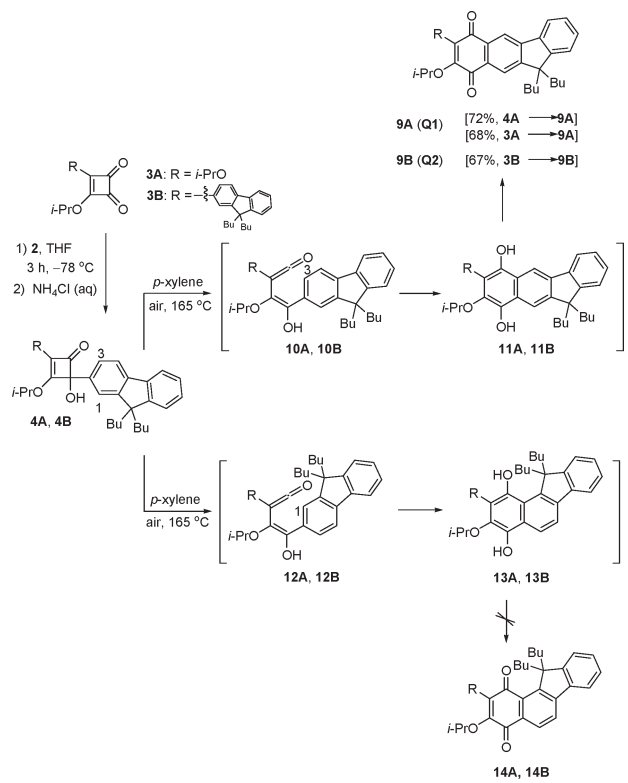
Having cyclobutenedione derivatives in hand, we next synthesized fluorenyl-substituted benzoquinones **9A** (**Q1**) and **9B** (**Q2**) (Scheme 3). Firstly, the solution of alcohol **4A** in *p*-xylene was heated at reflux for 3 h open to the air to promote the oxidation of hydroquinone **11A** to the benzoquinone **Q1**. After evaporation of *p*-xylene and column chromatography, **Q1** was isolated in 72% yield. A more practical approach to the benzoquinone **Q1** was achieved without isolation and purification of the intermediate alcohol **4A**. The crude material containing the alcohol **4A** obtained by the reaction of diisopropyl squarate **3A** with 2-lithio-9,9-dibutyl-fluorene **2** at −78 °C, followed by an ammonium chloride quench, was dissolved in *p*-xylene and then heated at reflux open to the air. In this way, fluorenyl-substituted benzoquinone **Q1** was produced in 68% overall yield from diisopropyl squarate **3A**. Similarly, the THF solution of




**Scheme 1** Synthesis of the cyclobutenedione derivative **3B** from diisopropyl squarate **3A**.




**Scheme 2** Synthetic route to the fluorene-bridged cyclobutenedione **8A** from diisopropyl squarate **3A**.

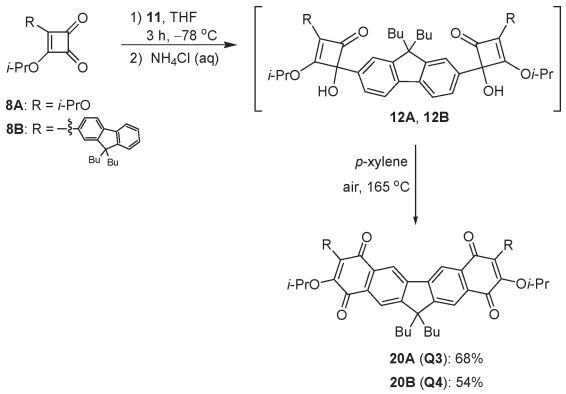



**Scheme 3** Synthetic routes to the linearly-fluorene-fused benzoquinone derivatives **Q1** and **Q2**.

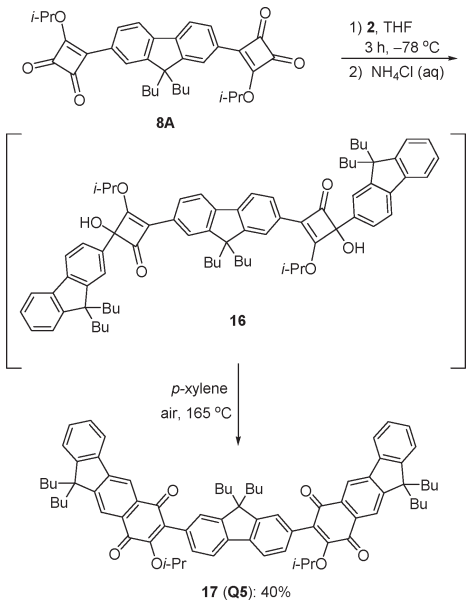
fluorenyl-substituted cyclobutenedione **3B** was reacted with 2-lithio-9,9-dibutyl-fluorene **2** at −78 °C for 3 h and followed by thermolysis of initially formed hydroxycyclobutenone **4B** to furnish the benzoquinone **Q2** in 67% yield. During heating, the colour of solution slowly turned from yellow to orange in 3 h, which indicated the formation of fluorescent benzoquinone **Q2**. Although the thermal rearrangement of the 4-fluorenyl-4-hydroxycyclobutenones (**4A** and **4B**) possibly occurs *via* a ring closure at two different positions (1 and 3) of the fluorenyl group, we obtained linearly-fluorene-fused benzoquinone derivatives **Q1** and **Q2** as the only products. The configuration of benzoquinone **Q2** was also determined by an X-ray crystal structure analysis (see Supporting Information†).[15]

The fluorene-fused benzoquinone derivatives **15A** (**Q3**) and **15B** (**Q4**) were prepared *via* reaction of 2.2 equiv. of cyclobutenediones **3A** and **3B** with 2,7-dilithio-9,9-dibutyl-fluorene **6**, followed by heating the initially formed hydroxycyclobutenones **7A** and **7B** at reflux open to the air (Scheme 4).

We also synthesized fluorene-bridged fluorene-fused benzoquinone **17** (**Q5**) in 40% yield by the treatment of cyclobutenedione **8A** with 2-lithio-9,9-dibutyl-fluorene **2** at −78 °C for 3 h and subsequent thermolysis of the intermediate fluorene-bridged hydroxycyclobutenone **16** in *p*-xylene (Scheme 5).




**Scheme 4** Synthetic routes to the fluorene-fused benzoquinones **Q3** and **Q4**.




**Scheme 5** Synthetic route to fluorene-bridged fluorene-fused benzoquinone **Q5**.

## Electrochemistry

Cyclic voltammograms were recorded for the derivatives **Q1**–**Q5** in dry $CH_3CN$ (0.2 M TBATFB) to investigate their redox behavior, and to ascertain the electrochemical reversibility of the quinone group(s). For brevity the case for **Q4** is discussed here but recorded potentials, referenced to the $Fc^+/Fc$ couple, for all derivatives are collected in Table 1. The oxidative portion of the cyclic voltammogram for **Q4** (see Supporting Information†) is dominated by an irreversible wave at $E_{ox}$ = +1.11 (*vs* $Fc^+/Fc$), which is taken to represent oxidation of the two periphery fluorene groups. Upon reductive scanning two closely spaced one-electron reversible waves are observed at $E_{1/2}$ = −1.06 V ($\Delta E$ = 60 mV) and $E_{1/2}$ = −1.17 V ($\Delta E$ = 60 mV) *vs.* $Fc^+/Fc$, which are associated with reduction of the two quinone units. The observed splitting of the two waves ($\Delta E_p$ = 110 mV) is highly supportive of the fact that the two quinone groups are in electronic communication *via* the fused fluorene group. The comproportionation constant ($\ln K_c = nF\Delta E_p/RT$) is 72.5. Upon further scanning to a more negative potential, a second quasi-reversible wave is seen for **Q4** at $E_{1/2}$ = −1.68 ($\Delta E$ = 130 mV) *vs.* $Fc^+/Fc$, presumably representing addition of a second electron to the semi-reduced quinone moiety.

The electrochemical behavior for the other derivatives is readily understood in terms of quinone reduction and fluorene oxidation. It is noticeable that the two quinone groups in **Q5** are reduced at the same potential, which suggests that the central fluorene unit insulates the two remote quinone subunits. Despite

**Table 1** Redox potentials collected for the quinone derivatives in $CH_3CN$ at a glassy carbon working electrode and a 50 mV $s^{-1}$ scan rate

| Compound | $E_{ox}$[a]/V | $E_{ox}$[b]/V | $E_{1/2}$[c]/V[e] | $E_{1/2}$[d]/V[e] | $\Delta E$[f]/V |
|---|---|---|---|---|---|
| **Q1** | +1.29 | — | −1.19 (60 mV) | −1.71 (70 mV) | 2.48 |
| **Q2** | +1.38 | +1.19 | −1.12 (60 mV) | −1.55 (80 mV) | 2.31 |
| **Q3** | — | — | −1.11 (60 mV)/−1.21 (60 mV) | −1.73 (120 mV) | — |
| **Q4** | — | +1.11 | −1.06 (60 mV)/−1.17 (60 mV) | −1.68 (130 mV) | 2.17/2.28 |
| **Q5** | +1.18 | +1.12 | −1.19 (70 mV) | −1.73 (80 mV) | 2.31 |

[a] Oxidation of fused fluorene unit. [b] Oxidation free to rotate fluorene unit. [c] Half-wave potential for first quinone redox couple. [d] Half-wave potential for second quinone redox couple. [e] Peak separation in brackets. [f] Difference between fluorene oxidation potential and quinone reduction potential.

the fusion of the fluorene unit to the quinone in **Q1** its oxidation (albeit irreversible) is still observed. However, the fusion of two quinone units to the fluorene (*i.e.*, **Q3** & **Q4**) renders its oxidation too difficult. By comparison of the cyclic voltammograms for the derivatives it is possible to assign the first oxidation wave for **Q2** and **Q4** to the free to rotate fluorene group. The main point to take notice of is the possibility for intramolecular charge transfer, in which an electron is transferred from the free to rotate fluorene to the quinone unit. Values for the separation ($\Delta E$) between the oxidation and reduction potentials are collected in Table 1, and further discussion of this matter will be made later on.

### Molecular orbital calculations

In an endeavour to support conclusions drawn from the electrochemical experiments *ab initio* molecular orbitals calculations were performed on the central quinones **Q1** and **Q2** using the suite of programs available in Gaussian-03.[16] To simplify the computer calculations methyl group(s) replaced the butyl groups and the isopropyl group in the two structures. The ground-state structures for the two quinone derivatives were in the first iteration calculated at the Hartree–Fock level and using the 6-311G basis set. Further refinement of the structures and more comprehensive determination of energies and locality of HOMO/LUMOs was performed using DFT with B3LYP and the 6-311G basis set. Calculated structures for **Q1** and **Q2** are presented in the Supporting Information† and the main point to note is the twisted alignment of the terminal fluorene unit in **Q2**. Concentrating firstly on **Q1** the HOMO is associated with the fluorene unit, although a fair proportion of electron density is also seen on the two linking carbon atoms. The LUMO is as expected focused primarily on the quinone group affording a HOMO–LUMO energy gap of 2.83 eV (22 825 $cm^{-1}$). The molecular orbital picture for **Q2** (Fig. 2) is revealing in that the HOMO is now associated with the terminal fluorene group and it is the HOMO-1 that resides on the fluorene subunit fused to the quinone (*cf.* **Q1**). These two results are consistent with the electrochemistry finding that the terminal fluorene is the easiest to oxidize. As in the case for the basic derivative the LUMO for **Q2** is associated with the quinone moiety and the corresponding HOMO–LUMO energy gap is 2.48 eV (19 972 $cm^{-1}$). It is encouraging that both the calculated HOMO–LUMO gaps are in remarkably good agreement with the electrochemistry determined $\Delta E$ values (Table 1).

### Basic photophysics

Despite the obvious lack of extended π-conjugation in the quinone derivatives, **Q1–Q5**, they are all red/yellow in colour. The absorption profiles collected at ambient temperature in $CH_3CN$ (see the Supporting Information†) all display relatively intense electronic transitions in the region below ~350 nm, which are presumably π–π* in nature for the fluorene subunit. The main focus is the longer-wavelength absorption profiles that stretch to around $\lambda_{ABS}$ = 550 nm, and we use the derivative **Q2** to highlight several points. Close inspection of the absorption spectrum for **Q2** in cyclohexane (Fig. 3) reveals that the lowest-energy band is Gaussian-like in shape centered around $\lambda_{ABS}$ = 467 nm ($\varepsilon_{max}$ = 4500 $M^{-1}$ $cm^{-1}$). This band is only just discernable in the spectrum for **Q2** in $CH_3CN$ and is located around $\lambda_{ABS}$ = 433 nm ($\varepsilon_{max}$ = 3000 $M^{-1}$ $cm^{-1}$). Selective illumination into the long-wavelength absorption profile in cyclohexane results in weak fluorescence centered at $\lambda_{EM}$ = 561 nm corresponding to a quantum yield ($\phi_F$) of 0.019. The rather large Stokes' shift (SS) of 3588 $cm^{-1}$ suggests that the vibrationally relaxed excited-state and ground-state structures are quite different. The room temperature emission for **Q2** in $CH_3CN$ is located at $\lambda_{EM}$ = 644 nm, and the SS is increased to 7567 $cm^{-1}$. It is apparent that the SS depends on the solvent such that it is larger in a more polar solvent. Such an observation is highly reminiscent of molecular systems that display charge transfer character,[17] and so to test this hypothesis absorption and emission spectra for **Q2** were recorded in a range of dissimilar polarity solvents (Table 2, Supporting Information†). It turned out that values for the SS (in $cm^{-1}$) could be adequately analyzed in terms of the Lippert-Mataga eqn (1) (Fig. 3), where '*a*' represents the radius of the spherical cavity in which the molecule resides and that is provided by a solvent dielectric continuum

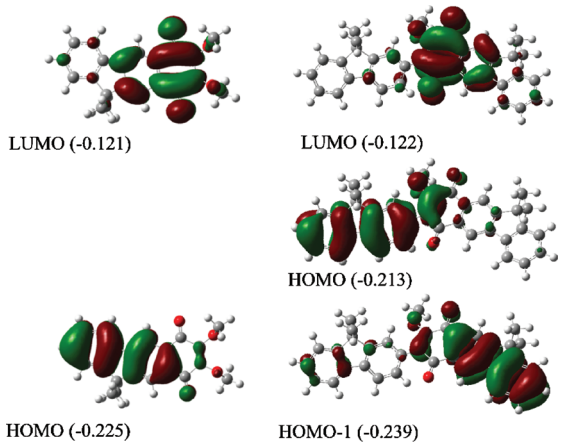



**Fig. 2** Visualization of selected molecular orbitals for **Q1** (left) and **Q2** (right) calculated using DFT (B3LYP) and the 6-311G basis set.

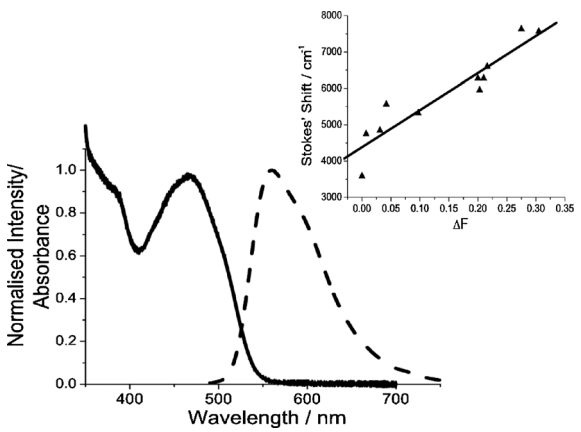



**Fig. 3** Absorption (solid) and emission (dash) profiles for **Q2** collected at room temperature in cyclohexane. Excitation wavelength $\lambda_{ex}$ = 425 nm. Insert shows the relationship between SS and the solvent Pekar function ($\Delta F$).

and $\mu_{gs}$ and $\mu_{ex}$ are the dipole moments for the ground-state and excited-state, respectively.[18]

$$SS = 10,070\left[\frac{(\mu_{ex}-\mu_{gs})^2}{a^3}\right]\Delta F + C \qquad (1)$$
$$\Delta F = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right]$$

Using the computer calculated $\mu_{gs}$ of 3.0 D, slope = 10 199 $cm^{-1}$ and $a$ = 9.5 Å (half the diameter for **Q2**) plus the calculated change in dipole moment using eqn (1) affords $\mu_{ex}$ = 32.5 D. This rather high value, but comparable with simple donor–acceptor systems,[19] would suggest that a significant fraction (~96%) of an electron is transferred upon formation of the excited state; this of course assumes that the distance is from the centroids of the donor fluorene to the quinone group (*ca.* 6.4 Å). The clear red/pink colour (Fig. 3) observable by eye under UV excitation of **Q2** in solution is consequently associated with emission from a charge transfer state. Extremely weak fluorescence is seen from both **Q1** and **Q3** at room temperature in cyclohexane ($\phi_F < 0.002$), whereas in comparison the emission is more pronounced from **Q4** ($\phi_F = 0.023$) and **Q5** ($\phi_F = 0.041$). However, it would appear that very little improvement in emission output is forthcoming by increasing the structural complexity of the quinone derivatives.

Having established the ground- and excited-state charge transfer character for **Q2** it is possible to calculate the total reorganization energy ($\lambda_{tot}$) in all the solvents given that SS = $2\lambda_{tot}$.[20] The parameter $\lambda_{tot}$ represents the summation of contributions from the solvent reorganization energy ($\lambda_{solv}$) and vibrational reorganization energy ($\lambda_{vib}$) in supporting formation of the charge transfer state. This later parameter can be obtained from analysis of the resonance Raman spectrum for CT complexes,[21] but no attempt was made to do this for **Q2**. Nevertheless, there is a very noticeable correlation between $\lambda_{tot}$ and the dielectric constant ($\varepsilon$) for the solvents studied (Fig. 4), reaching a plateau of around 0.47 eV for highly polar solvents. From theory $\lambda_{solv}$ is related to the solvent coupling parameter $C$ by the equation:

$$\lambda_{Solv} = e^2 C(1/2a_1 + 1/2a_2 - 1/R)\ C = 1/\varepsilon_{op} - 1/\varepsilon_{st}$$

where $\varepsilon_{op}$ and $\varepsilon_{st}$ are the optical and static dielectric constants of the solvent and $a_1$ and $a_2$ are the radii of the two reactants, and $R$ is the separation distance.[22] The rather good correlation between $\lambda_{tot}$ and $1/\varepsilon$ (Fig. 4) is presumably indicating that $\lambda_{vib}$ is not varying widely with solvent polarity.

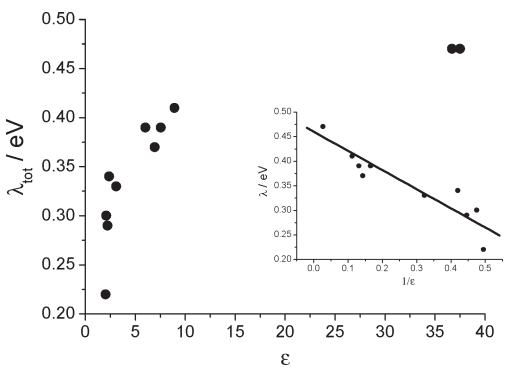



**Fig. 4** Relationship between the total reorganization energy ($\lambda_{tot}$) and the solvent dielectric constant ($\varepsilon$) for **Q2**. Insert shows the data re-plotted in its linear form as $1/\varepsilon$.

### Turn-on ROS response

Fluorescence detection of ROS is often associated with a redox change at a periphery site that is coupled to the fluorophore.[23] Modulation in fluorescence intensity is the signal for any interaction of the ROS with the probe, often by inhibiting intramolecular quenching processes such as photoinduced electron transfer.[9a] It is clear that the quinone resting state for the derivatives discussed here is the incorrect oxidation state for reaction with any type of ROS. Essentially, the required hydroquinone solid sample is partially unstable towards oxidation and so it is not possible to isolate pure samples of the required compounds. At first, this incompatibility between the quinone/hydroquinone forms does not fit in with the requirement for a successful ROS probe. However, it was noticed that an *in situ* reduction of the quinone for **Q2** (and **Q4**–**Q5**) resulted in an alteration in fluorescence colour from red to blue. Instead of the customary on/off fluorescence response[24] the molecular systems remain bright and transform between two easily distinguishable colours. Such a response is rather unique since often excited-state quenching by electron/energy transfer will successfully compete with radiative decay, and essentially "dull" the fluorescence colour response. Thus, as a new concept it is proposed that prior to ROS detection the probe is firstly switched on (blue fluorescence) and then allowed to detect any oxy radical species by reappearance of the red fluorescence colour. To test this hypothesis **Q2** was dispersed in distilled water containing Triton-X100 (5% w/v) at a concentration to achieve micelle formation. The fluorescence profile collected on the dispersion is illustrated in Fig. 5, along with a picture of the sample under UV excitation ($\lambda$ > 350 nm). The

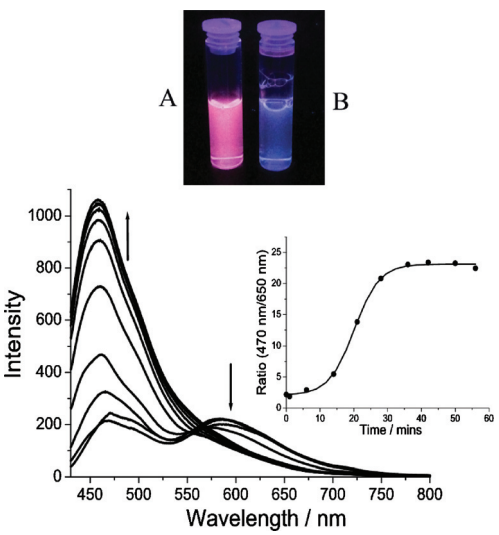



**Fig. 5** Alteration in the fluorescence profiles for **Q2** dispersed in water (0.2 M $Na_2HPO_4$) containing Triton-X100 (5% w/v) after the addition of sodium ascorbate. Insert shows the change in the ratio of absorbance at 470 nm and 650 nm over time. Top picture show the change in fluorescence colour change over time (A = initial, B = final).

typical red fluorescence is clearly observed along with the broad emission profile centered at around $\lambda_{EM}$ = 587 nm. Upon addition of sodium ascorbate the fluorescence spectrum undergoes a change in appearance, with a grow-in of a new emission at $\lambda_{EM}$ = 470 nm and a concomitant decrease at $\lambda_{EM}$ = 587 nm. The change over time is readily represented in a ratiometric manner as shown in the insert of Fig. 5. In addition, the red fluorescence colour fades and is replaced by the blue colour for the hydroquinone form. The blue colour remains even in the presence of oxygen, suggesting that the hydroquinone is stable enough for subsequent reactions. The system is reversible since the addition of sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$), acting as the ROS source, brings about the reordering of the fluorescence colour. At this stage no attempt was made to optimize the turn on time of the probe, which is possibly limited by penetration and reaction of the ascorbate into the micelle structure.

## Conclusions

The fusion of a fluorene with a benzoquinone produces a new variety of an electron-accepting quinone-based moiety. The appending of a second electron-donating fluorene unit creates a molecule that displays ground-state charge transfer, and formation of a weakly emissive charge-transfer state following excitation. The unmistakable red emission can be switched to blue by straightforward reduction of the quinone group, and the process is reversed by oxidation of the hydroquinone with peroxide. Because of the inherent flexibility in the synthesis it is conceivable that fluorescence colour could be tuned further to the red by altering the oxidation potential of the donor fluorene group. Alternatively, to produce more emissive molecular systems replacement of fluorene with more specialized electron donors may be necessary. Even though the molecular system tested could be uptaken into a micelle in water, to impose specialized localization in a cell will require added sophistication to the structure. We expect to test this idea in new amphiphilic derivatives.

## Experimental section

### General

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. 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. NMR spectra were recorded with a Bruker AM 250 (250 MHz for $^1$H and 62.9 MHz for $^{13}$C NMR), a Bruker Spectrospin Avance DPX400 Ultrashield (400 MHz for $^1$H and 100.59 MHz for $^{13}$C NMR) and Varian Inova 600 (600 MHz for $^1$H and 150 MHz for $^{13}$C NMR) instruments. Chemical shifts $\delta$ were given in ppm relative to residual peaks of deuterated solvents (adjusted to 7.26 ppm for $^1$H NMR and 77.0 for $^{13}$C NMR) and coupling constants, $J$, were given in Hertz. The following abbreviations are used to describe spin multiplicities in $^1$H NMR spectra: s = singlet; bs = broad singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; spt = septet; m = multiplets. Multiplicities in $^{13}$C NMR spectra were determined by DEPT (Distortionless Enhancement by Polarization Transfer) or APT (Attached Proton Test) measurements and were given as ($C_{quat}$, CH, $CH_2$, $CH_3$). 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 Spectrometer (Thermo Finnigan). High resolution mass spectra (HRMS) were obtained on a Waters Synapt Q-TOF-MS spectrometer. The following compounds were prepared according to known literature methods: 2-bromo-9,9-dibutyl-fluorene,[25] 2,7-dibromo-9,9-dibutyl-fluorene.[26]

Absorption spectra were recorded using a Hitachi U3310 spectrophotometer and corrected fluorescence spectra were recorded using a Lambda Advanced F 4500 spectrometer. Cyclic voltammetry experiments were performed using a fully automated HCH Instruments Electrochemical Analyzer and a three-electrode set-up consisting of a glassy carbon working electrode, a platinum wire counter electrode and a silver wire reference electrode. Ferrocene was used an internal standard. All studies were performed in deoxygenated $CH_3CN$ containing TBATFB (0.2 M) as background electrolyte. The solute concentrations were typically 0.1 mM. Redox potentials were reproducible to within ±15 mV.

All luminescence measurements were made using optically dilute solutions and were corrected for spectral imperfections of the instrument by reference to a standard lamp. Solvent-corrected luminescence quantum yields were measured relative to $[Ru(bipy)_3]^{2+}$ in acetonitrile[27] using optically matched solutions and were measured twice for consistency in calculated values.

### Synthesis of cyclobutenedione derivatives 3B, 4A and 8A:

**4-(9′,9′-dibutyl-9′*H*-fluoren-2′-yl)-4-hydroxy-2,3-diisopropoxy-cyclobut-2-enone (4A).** To a solution of 2-bromo-9,9-dibutyl-fluorene (**1**, 4.5 g, 12.6 mmol, 1.1 eq.) in THF (45 mL) at −78 °C under nitrogen, *n*-BuLi (6.9 mL of a 2.5 M of hexane solution, 17.4 mmol, 1.38 eq.) 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 3,4-diisopropoxy-3-cyclobutene-1,2-dione (**3A**, 2.25 g, 11.4 mmol, 1 eq.) in THF (45 mL) at −78 °C under the nitrogen atmosphere. After stirring for 3 h at −78 °C and 0.5 h at 0 °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 was concentrated in a rotary evaporator and the remaining crude material was subjected to chromatography on silica gel using 4 : 1 hexane/ethyl acetate as eluent to yield **4A** (4.66 g, 86%, yellow solid). Mp 66–67 °C, $R_f$ 0.23 (hexane/ethyl acetate 4 : 1); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 0.52–0.60 (m, 4 H, 2 × $CH_2$), 0.62–0.66 (m, 6 H, 2 × $CH_3$), 0.98–1.08 (m, 4 H, 2 × $CH_2$), 1.26 (d, $J$ = 8.0 Hz, 3 H, *i*PrO [$CH_3$]), 1.30 (d, $J$ = 8.0 Hz, 3 H, *i*PrO [$CH_3$]), 1.33 (d, $J$ = 8.0 Hz, 3 H, *i*PrO [$CH_3$]), 1.36 (d, $J$ =

8.0 Hz, 3 H, *i*PrO [$CH_3$]), 1.87–1.99 (m, 4 H, 2 × $CH_2$), 3.72 (bs, 1 H, OH), 4.84 (spt, $J$ = 8.0 Hz, 1 H, *i*PrO [CH]), 4.93 (spt, $J$ = 8.0 Hz, 1 H, *i*PrO [CH]), 7.21–7.28 (m, 3 H, Ar), 7.41–7.45 (m, 2 H, Ar), 7.59–7.63 (m, 2 H, Ar). $^{13}$C-NMR (100.59 MHz, $CDCl_3$, $CCl_4$): $\delta$ = 13.92 (2 × $CH_3$), 22.50 ($CH_2$), 22.65 ($CH_2$), 22.84 ($CH_3$, *i*PrO [$CH_3$]), 22.85 ($CH_3$, *i*PrO [$CH_3$]), 23.07 ($CH_3$, *i*PrO [$CH_3$]), 23.10 ($CH_3$, *i*PrO [$CH_3$]), 25.98 (2 × $CH_2$), 40.19 ($CH_2$), 40.22 ($CH_2$), 54.97 ($C_{quat}$), 73.46 (2 × CH, *i*PrO), 87.64 ($C_{quat}$), 119.70, 119.84, 120.34, 122.74, 124.70, 126.83, 127.18, 133.15, 136.86, 138.85, 140.73, 141.11, 150.81, 150.86, 184.07 ($C_{quat}$; C═O). IR (ATR): $\tilde{\nu}$ = 3349 (m), 2977 (m), 2931 (m), 2871 (w), 1765 (s), 1601 (vs), 1466 (s), 1383 (vs), 1373 (vs), 1205 (w), 1158 (w), 1094 (vs), 1035 (s), 945 (s), 906 (m), 816 (m). HRMS [TOF MS ES+]: $m/z$ [$M^+$ + Na] calcd. for $C_{31}H_{40}O_4Na$ 499.2824, found 499.2822 (−0.4 ppm).

**3-(9′,9′-Dibutyl-9′*H*-fluoren-2′-yl)-4-isopropoxycyclobut-3-en-1,2-dione (3B).** To a solution of **4A** (4.66 g, 9.78 mmol) in $CH_2Cl_2$ (30 mL), 5 drops of concentrated HCl were added. After stirring for 0.5 h at room temperature, water (50 mL) was added into the reaction mixture and was extracted with ether (100 mL). The organic layer was separated and dried over $Na_2SO_4$ and filtered. The solution was concentrated in a rotary evaporator and the remaining crude material was subjected to chromatography on silica gel using 10 : 1 hexane/ethyl acetate as eluent to yield **3B** (4.07 g, 100%, yellow solid). Mp 76–77 °C, $R_f$ 0.29 (hexane/ethyl acetate 10 : 1); $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 0.50–0.69 (m, 4 H, 2 × $CH_2$), 0.66 (t, $J$ = 7.3 Hz, 6 H, 2 × $CH_3$), 1.00–1.15 (m, 4 H, 2 × $CH_2$), 1.59 (d, $J$ = 6.3 Hz, 6 H, 2 × *i*PrO [$CH_3$]), 1.93–2.09 (m, 4 H, 2 × $CH_2$), 5.65 (spt, $J$ = 6.3 Hz, 1 H, *i*PrO [CH]), 7.39 (bs, 3 H, Ar), 7.75–7.78 (m, 1 H, Ar), 7.80–8.03 (AB system, $\delta_A$ = 8.01, $\delta_B$ = 7.83, $J_{AB}$ = 7.9 Hz, 2 H, Ar), 8.09 (s, 1 H, Ar). $^{13}$C-NMR (100.59 MHz, $CDCl_3$): $\delta$ = 13.51 (2 × $CH_3$), 22.71 (2 × $CH_3$, *i*PrO [$CH_3$]), 22.79 (2 × $CH_2$), 25.75 (2 × $CH_2$), 39.65 (2 × $CH_2$), 55.10 ($C_{quat}$), 79.68 (CH, *i*PrO), 120.03, 120.44, 121.68, 122.88, 126.43, 126.76, 126.91, 128.46, 139.58, 145.56, 151.25, 151.58, 174.23, 191.80, 192.94, 193.48, IR (ATR): $\tilde{\nu}$ = 2954 (m), 2928 (m), 2858 (m), 1780 (s), 1740 (s), 1584 (s), 1488 (w), 1422 (w), 1330 (m), 1277 (w), 1095 (m), 1078 (m), 1014 (m), 900 (m), 740 (s), HRMS [TOF MS ES+]: $m/z$ [$M^+$ + Na] calcd. for $C_{28}H_{32}O_3Na$ 439.2249, found 499.2261 (2.7 ppm).

**9,9-Dibutyl-2,7-bis(4-isopropoxycyclobut-3-en-1,2-dione-3-yl)-9*H*-fluorene (8A).** To a solution of 2,7-dibromo-9,9-dibutylfluorene (**5**, 3.0 g, 6.9 mmol, 1.0 eq.) in THF (40 mL) at −78 °C under nitrogen, *n*-BuLi (9.5 mL of a 1.6 M of hexane solution, 15.0 mmol, 2.2 eq.) 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 3,4-diisopropoxy-3-cyclobutene-1,2-dione (**3A**, 3.00 g, 15.0 mmol, 2.2 eq.) in THF at −78 °C under the nitrogen atmosphere. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% $NH_4Cl$ (50 mL) solution at −78 °C and then allowed to warm to rt. The mixture was diluted with ether (200 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 was concentrated in a rotary evaporator and the remaining crude material was dissolved in $CH_2Cl_2$ (40 mL). To this solution at room temperature, 5 drops of concentrated HCl were added. After stirring for 0.5 h at room temperature, water (50 mL) was added into the reaction mixture and extracted with ether (100 mL). The organic layer was separated and dried over $Na_2SO_4$ and filtered. The solution was concentrated in a rotary evaporator and the remaining crude material was subjected to chromatography on silica gel using 4 : 1 hexane/ethyl acetate as eluent to yield **8A** (3.17 g, 83%, yellow solid). Mp 208–209 °C, $R_f$ 0.39 (hexane/ethyl acetate 4 : 1); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 0.50–0.58 (m, 4 H, 2 × $CH_2$), 0.65 (t, $J$ = 7.3 Hz, 6 H, 2 × $CH_3$), 1.03–1.12 (m, 4 H, 2 × $CH_2$), 1.60 (d, $J$ = 6.2 Hz, 12 H, 4 × *i*PrO [$CH_3$]), 2.05–2.09 (m, 4 H, 2 × $CH_2$), 5.65 (spt, $J$ = 6.2 Hz, 2 H, 2 × *i*PrO [CH]), 7.88 (d, $J$ = 7.9 Hz, 2 H, Ar), 8.03–8.05 (m, 2 H, Ar), 8.09 (bs, 2 H, Ar). $^{13}$C-NMR (100.59 MHz, $CDCl_3$): $\delta$ = 13.75 ($CH_3$), 22.85 ($CH_2$), 22.08 (2 × CH3, *i*PrO [$CH_3$]), 25.98 ($CH_2$), 39.69 ($CH_2$), 55.75 ($C_{quat}$), 80.27 (CH, *i*PrO), 121.21, 121.95, 127.07, 127.90, 144.07, 152.50, 173.92, 192.14, 192.91, 194.02, IR (ATR): $\tilde{\nu}$ = 2931 (w), 2854 (w), 1780 (s), 1741 (s), 1583 (s), 1466 (m), 1421 (w), 1374 (s), 1342 (s), 1330 (m), 1272 (w), 1095 (m), 1078 (m), 1014 (m), 897 (m). Ms (APCI) $m/z$ (%): 555 (100) [$M^+$ + H], 513 (73), 471 (20), 415 (15), 359 (9), 303 (10). HRMS [TOF MS ES+]: $m/z$ [$M^+$ + Na] calcd. for $C_{35}H_{38}O_6Na$ 577.2566, found 577.2562 (−0.7 ppm).

**Synthesis of benzoquinone derivatives 9A–B, 15A–B, 17:**

**11,11-Dibutyl-7,8-diisopropoxy-11*H*-benzo[*b*]fluorene-6,9-dione (9A)**

**Starting from 4A.** The solution of **4A** (0.5 g) in *p*-xylene (15 mL) was heated at reflux open to the air in a preheated oil bath (165 °C) for 3 h. After removal of *p*-xylene in a rotary evaporator, the residue was subjected to chromatography on silica gel (*silica gel was firstly washed with $Et_3N$ and then several times with a mixture of hexane/ethyl acetate, 10 : 1*) using 10 : 1 hexane/ethyl acetate as eluent to yield **14A** (0.36 g, 72%, orange oil).

**Starting from 3A.** To a solution of 2-bromo-9,9-dibutylfluorene (**1**, 1.5 g, 4.2 mmol, 1.0 eq.) in THF (15 mL) at −78 °C under nitrogen, *n*-BuLi (2.3 mL of a 2.5 M of hexane solution, 5.8 mmol, 1.38 eq.) 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 3,4-diisopropoxy-3-cyclobutene-1,2-dione (**3A**, 0.75 g, 3.8 mmol, 0.9 eq.) in THF (15 mL) at −78 °C under the nitrogen atmosphere. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% $NH_4Cl$ (10 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 was concentrated in a rotary evaporator 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 3 h. After removal of the *p*-xylene in a rotary evaporator, the residue was subjected to chromatography on silica gel (*silica gel was firstly washed with $Et_3N$ and then several times with mixture of hexane/ethyl acetate, 10 : 1*) using 10 : 1 hexane/ethyl acetate as eluent to

yield **9A** (1.22 g, 68%, orange oil). $R_f$ 0.45 (hexane/ethyl acetate 10 : 1); $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 0.51–0.59 (m, 4 H, 2 × $CH_2$), 0.65 (t, $J$ = 7.3 Hz 6 H, 2 × $CH_3$), 1.02–1.11 (m, 4 H, 2 × $CH_2$), 1.37 (d, $J$ = 6.2 Hz, 3 H, *i*PrO [$CH_3$]), 1.38 (d, $J$ = 6.1 Hz, 3 H, *i*PrO [$CH_3$]), 1.97–2.10 (m, 4 H, 2 × $CH_2$), 4.92–5.00 (m, 2 H, *i*PrO [CH]), 7.36–7.41 (m, 3 H, Ar), 7.83–7.85 (m, 1 H, Ar), 8.02 (s, 1 H, Ar), 8.35 (s, 1 H, Ar),$^{13}$C-NMR (100.59 MHz, $CDCl_3$): $\delta$ = 13.70 (2 × $CH_3$), 22.80 ($CH_3$, 2 × *i*PrO [$CH_3$]), 22.85 ($CH_3$, 2 × *i*PrO [$CH_3$]), 22.91 (2 × $CH_2$), 25.96 (2 × $CH_2$), 39.84 (2 × $CH_2$), 55.95 ($C_{quat}$), 76.28 (CH, *i*PrO), 76.36 (CH, *i*PrO), 117.44 (CH), 120.62 (CH), 121.25 (CH), 123.09 (CH), 127.37 (CH), 129.07 (CH), 130.05 ($C_{quat}$), 131.08 ($C_{quat}$), 139.19 ($C_{quat}$), 146.66 ($C_{quat}$), 148.20 ($C_{quat}$), 148.49 ($C_{quat}$), 151.65 ($C_{quat}$), 156.49 ($C_{quat}$), 182.95 ($C_{quat}$; C═O), 182.97 ($C_{quat}$; C═O). IR (ATR): $\tilde{\nu}$ = 2958 (m), 2928 (m), 2858 (m), 1656 (s), 1600 (s), 1564 (m), 1465 (m), 1374 (w), 1357 (w), 1326 (m), 1280 (m), 1188 (s), 1167 (s), 1093 (s), 997 (s), 906 (m), 738 (s), Ms (70 eV, ESI) *m*/*z* (%): 475 (100) [$M^+$ + H], 459 (27), 433 (12), 396 (26). HRMS [TOF MS ES+]: *m*/*z* [$M^+$ + Na] calcd. for $C_{31}H_{38}O_4Na$ 497.2668, found 497.2663 (−1.0 ppm).

**11,11-Dibutyl-7-(9′,9′-dibutyl-*9′H*-fluoren-2′-yl)-8-isopropoxy-11H benzo[*b*]fluorene-6,9-dione (9B).** To a solution of 2-bromo-9,9-dibutyl-fluorene (**1**, 1.13 g, 3.2 mmol, 1.0 eq.) in THF (15 mL) at −78 °C under nitrogen, *n*-BuLi (1.75 mL of a 2.5 M of hexane solution, 4.4 mmol, 1.38 eq.) was added *via* syringe in 15 min. The resulting mixture was stirred at −78 °C for 1 h and then transferred *via* cannula to a solution of **3B** (1.19 g, 2.9 mmol, 0.9 eq.) in THF (15 mL) at −78 °C under the nitrogen atmosphere. After stirring fore 3 h at −78 °C, the reaction mixture was quenched with 10% $NH_4Cl$ (10 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 was concentrated in a rotary evaporator 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 3 h. After removal of the *p*-xylene in a rotary evaporator, the residue was subjected to chromatography on silica gel (*silica gel was firstly washed with $Et_3N$ and then several times with mixture of hexane/ethyl acetate, 10 : 1*) using 10 : 1 hexane/ethyl acetate as eluent to yield **9B** (1.33 g, 67%, orange solid). Mp 165–166 °C, $R_f$ 0.53 (hexane/ethyl acetate 10 : 1), $^1$H-NMR (600 MHz, $CDCl_3$): $\delta$ = 0.54–0.60 (m, 4 H, 2 × $CH_2$), 0.62–0.72 (m, 16 H, 2 × $CH_2$, 4 × $CH_3$), 1.06–1.11 (m, 8 H, 4 × $CH_2$), 1.38 (d, $J$ = 5.9 Hz, 6 H, 2 × *i*PrO [$CH_3$]), 1.97–2.00 (m, 4 H, 2 × $CH_2$), 2.01–2.09 (m, 4 H, 2 × $CH_2$), 4.70–4.73 (m, 1 H, *i*PrO [CH]), 7.33–7.42 (m, 8 H, Ar), 7.73–7.88 (m, 3 H, Ar), 8.09 (s, 1 H, Ar), 8.45 (s, 1 H, Ar),$^{13}$C-NMR (150.83 MHz, $CDCl_3$): $\delta$ = 13.74 (2 × $CH_3$), 13.82 (2 × $CH_3$), 22.69 (2 × $CH_2$), 22.93 (2 × $CH_2$), 23.09 (2 × $CH_3$, *i*PrO [$CH_3$]), 25.97 (2 × $CH_2$), 26.01 (2 × $CH_2$), 39.92 (2 × $CH_2$), 40.21 (2 × $CH_2$), 55.05 ($C_{quat}$), 55.92 ($C_{quat}$), 76.66 (CH, *i*PrO), 117.88 (CH), 118.88 (CH), 119.89 (CH), 120.48 (CH), 121.40 (CH), 122.87 (CH), 123.09 (CH), 125.47 (CH), 126.78 (CH), 127.28 (CH), 127.41 (CH), 129.18 (CH), 129.62 (CH), 129.81 ($C_{quat}$), 130.43 ($C_{quat}$), 132.19 ($C_{quat}$), 135.04 ($C_{quat}$), 139.28 ($C_{quat}$), 140.79 ($C_{quat}$), 141.31 ($C_{quat}$), 147.05 ($C_{quat}$), 149.74 ($C_{quat}$), 151.14 ($C_{quat}$), 151.72 ($C_{quat}$), 156.16 ($C_{quat}$), 156.20 ($C_{quat}$), 182.74 ($C_{quat}$; C═O), 185.29 ($C_{quat}$; C═O). IR (ATR): $\tilde{\nu}$ = 2954 (m), 2927 (m), 2857 (m), 1662 (s), 1652 (s), 1464 (m), 1450 (m), 1374 (w), 1359 (w), 1317 (s), 1293 (m), 1280 (m), 1165 (m), 1098 (s), 1020 (m), 914 (w), 740 (s), Ms (APCI) *m*/*z* (%): 692 (100) [$M^+$], 651 (20). HRMS [TOF MS ES+]: *m*/*z* [$M^+$ + Na] calcd. for $C_{49}H_{56}O_3Na$ 715.4127, found 715.4152 (3.5 ppm).

**12,12-Dibutyl-2,3,8,9-tetraisopropoxy-12*H*-dibenzo[*b*,*h*]fluorene-1,4,7,10-tetrone (15A)**

To a solution of 2,7-dibromo-9,9-dibutyl-fluorene (**5**, 3.0 g, 6.9 mmol, 1.0 eq.) in THF (40 mL) at −78 °C under nitrogen, *n*-BuLi (9.5 mL of a 1.6 M of hexane solution, 15.0 mmol, 2.2 eq.) 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 **3A** (3.0 g, 15.0 mmol, 2.2 eq.) in THF (60 mL) at −78 °C under the nitrogen atmosphere. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% $NH_4Cl$ (50 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 was concentrated in a rotary evaporator and the remaining crude material was dissolved in *p*-xylene (50 mL). The resulting solution was heated at reflux open to the air in a preheated oil bath (165 °C) for 3 h. After removal of the *p*-xylene in a rotary evaporator, the residue was subjected to chromatography on silica gel (*silica gel was firstly washed with $Et_3N$ and then several times with mixture of hexane/ethyl acetate, 10 : 1*) using 10 : 1 hexane/ethyl acetate as eluent to yield **15A** (3.13 g, 68%, yellow solid). Mp 98–99 °C, $R_f$ 0.30 (hexane/ethyl acetate 10 : 1), $^1$H-NMR (600 MHz, $CDCl_3$): $\delta$ = 0.50–0.59 (m, 2 H, $CH_2$), 0.65 (t, $J$ = 7.0 Hz 3 H, $CH_3$), 1.06–1.09 (m, 2 H, $CH_2$), 1.39 (d, $J$ = 6.5 Hz, 3 H, *i*PrO [$CH_3$]), 1.40 (d, $J$ = 5.8 Hz, 3 H, *i*PrO [$CH_3$]), 2.10–2.35 (m, 2 H, $CH_2$), 4.95–5.03 (m, 2 H, *i*PrO [CH]), 8.07 (s, 1 H, Ar), 8.51 (s, 1 H, Ar), $^{13}$C-NMR (150.83 MHz, $CDCl_3$): $\delta$ = 13.70 ($CH_3$), 22.82 ($CH_3$, *i*PrO [$CH_3$]), 22.85 ($CH_3$, *i*PrO [$CH_3$]), 22.86 ($CH_2$), 26.05 ($CH_2$), 39.68 ($CH_2$), 56.99 ($C_{quat}$), 76.44 (CH, *i*PrO), 76.53 (CH, *i*PrO), 119.09 (CH), 120.81 (CH), 130.35 ($C_{quat}$), 131.38 ($C_{quat}$), 144.37 ($C_{quat}$), 148.42 ($C_{quat}$), 148.47 ($C_{quat}$), 157.10 ($C_{quat}$), 182.34 ($C_{quat}$; 2 × C═O), 182.70 ($C_{quat}$; 2 × C═O). IR (ATR): $\tilde{\nu}$ = 2960 (w), 2929 (w), 2859 (w), 1655 (s), 1600 (s), 1567 (m), 1465 (w), 1374 (w), 1318 (w), 1281 (m), 1201 (s), 1163 (s), 1092 (s), 1003 (s), 974 (s), 905 (m), 734 (m), Ms (APCI) *m*/*z* (%): 671 (100) [$M^+$ + H], 629 (11). HRMS [APCI]: *m*/*z* [$M^+$ + H] calcd. for $C_{41}H_{51}O_8$ 671.3587, found 671.3605 (3.5 ppm).

**12,12-Dibutyl-3,8-di(9′,9′-dibutyl-9′*H*-fluoren-2′-yl)-2,9-diisopropoxy-12*H*-dibenzo[*b*,*h*]fluorene-1,4,7,10-tetrone (15B).** To a solution of 2,7-dibromo-9,9-dibutyl-fluorene (**5**, 0.38 g, 0.87 mmol, 1.0 eq.) in THF (15 mL) at −78 °C under nitrogen, *n*-BuLi (0.82 mL of a 2.5 M of hexane solution, 2.09 mmol, 2.4 eq.) was added *via* syringe in 15 min. The resulting mixture was stirred at −78 °C for 1 h and then transferred *via* cannula to a

solution of **3B** (0.8 g, 1.92 mmol, 2.2 eq.) in THF (20 mL) at −78 °C under the nitrogen atmosphere. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% $NH_4Cl$ (10 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 was concentrated in a rotary evaporator 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 3 h. After removal of the *p*-xylene in a rotary evaporator, the residue was subjected to chromatography on silica gel (*silica gel was firstly washed with $Et_3N$ and then several times with mixture of hexane/ethyl acetate, 10 : 1*) using 10 : 1 hexane/ethyl acetate as eluent to yield **15B** (0.54 g, 54%, orange solid). Mp 152–153 °C, $R_f$ 0.47 (hexane/ethyl acetate 10 : 1) $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 0.58–0.72 (m, 30 H, 6 × $CH_2$, 6 × $CH_3$), 1.07–1.18 (m, 12 H, 6 × $CH_2$), 1.16 (d, $J$ = 6.0 Hz, 12 H, 4 × *i*PrO [$CH_3$]), 2.00 (t, $J$ = 7.8 Hz, 8 H, 4 × $CH_2$), 2.17–2.27 (m, 4 H, 2 × $CH_2$), 4.69–4.79 (m, 2 H, 2 × *i*PrO [CH]), 7.37–7.45 (m, 10 H, Ar), 7.75–7.82 (m, 4 H, Ar), 8.18 (s, 2 H, Ar), 8.68 (s, 2 H, Ar). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): $\delta$ = 13.71 ($CH_3$), 13.80 (2 × $CH_3$), 22.71 ($CH_3$, *i*PrO [$CH_3$]), 22.88 ($CH_2$), 23.09 (2 × $CH_2$), 26.05 (2 × $CH_2$), 26.14 ($CH_2$), 39.81 ($CH_2$), 40.21 (2 × $CH_2$), 55.10 ($C_{quat}$), 56.97 ($C_{quat}$), 76.80 (CH, *i*PrO), 118.95, 119.72, 119.95, 120.71, 122.89, 125.52, 126.83, 127.38, 128.89, 129.59, 131.87, 132.58, 135.35, 140.77, 141.54, 144.85, 149.84, 151.20, 156.19, 156.86, 182.54 ($C_{quat}$; C═O), 184.66 ($C_{quat}$; C═O). IR (ATR): $\tilde{\nu}$ = 2955 (m), 2928 (s), 2858 (m), 1662 (vs), 1604 (s), 1563 (m), 1453 (s), 1295 (vs), 1194 (m), 1159 (m), 1081 (m), 1023 (vs), 1006 (w), 903 (m), 737 (vs). Ms (APCI) *m*/*z* (%): 1107.8 (100) [$M^+$ + H].

**2,7-Bis(11′,11′-dibutyl-8′-isopropoxy-11′*H*-benzo[*b*]fluorene-6′,9′-dione-7′-yl)-9,9-dibutyl-fluorene (17).** To a solution of 2-bromo-9,9-dibutyl-fluorene (**1**, 1.0 g, 2.8 mmol, 2.2 eq.) in THF (25 mL) at −78 °C under nitrogen, *n*-BuLi (1.9 mL of a 2.5 M of hexane solution, 3.0 mmol, 2.4 eq.) 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 **8A** (0.71 g, 1.3 mmol, 1.0 eq.) in THF (55 mL) at −78 °C under the nitrogen atmosphere. After stirring for 3 h at −78 °C, the reaction mixture was quenched with 10% $NH_4Cl$ (10 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 was concentrated in a rotary evaporator and the remaining crude material was dissolved in *p*-xylene (40 mL). The resulting solution was heated at reflux open to the air in a preheated oil bath (165 °C) for 2 h. After removal of the *p*-xylene in a rotary evaporator, the residue was subjected to chromatography on silica gel (*silica gel was firstly washed with $Et_3N$ and then several times with mixture of hexane/ethyl acetate, 10 : 1*) using 10 : 1 hexane/ethyl acetate as eluent to yield **17** (**Q5**) (0.56 g, 40%, red solid). Mp 143–144 °C, $R_f$ 0.40 (hexane/ethyl acetate 10 : 1), $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 0.61–0.86 (m, 30 H, 6 × $CH_2$, 6 × $CH_3$), 1.03–1.18 (m, 12 H, 6 × $CH_2$), 1.17 (d, $J$ = 6.2 Hz, 12 H, 4 × *i*PrO [$CH_3$]), 2.04–2.10 (m, 12 H, 6 × $CH_2$), 4.70–4.80 (m, 2 H, 2 × *i*PrO [CH]), 7.42–7.47 (m, 10 H, Ar), 7.83–7.91 (m, 4 H, Ar), 8.12 (s, 2 H, Ar), 8.48 (s, 2 H, Ar).$^{13}$C-NMR (62.9 MHz, $CDCl_3$): $\delta$ = 13.72 (2 × $CH_3$), 13.84 ($CH_3$), 22.74 ($CH_3$, *i*PrO [$CH_3$]), 22.94 (2 × $CH_2$), 23.17 ($CH_2$), 26.01 (2 × $CH_2$), 26.14 ($CH_2$), 39.92 (2 × $CH_2$), 40.28 ($CH_2$), 55.23 ($C_{quat}$), 55.95 ($C_{quat}$), 76.72 (CH, *i*PrO), 117.89 (CH), 119.15(CH), 120.52 (CH), 121.42 (CH), 123.12 (CH), 125.57 (CH), 127.43 (CH), 129.19 (CH), 129.79 (CH), 130.23 ($C_{quat}$), 130.49 ($C_{quat}$), 132.24 ($C_{quat}$), 135.02 ($C_{quat}$), 139.33 ($C_{quat}$), 141.04 ($C_{quat}$), 147.09 ($C_{quat}$), 150.27 ($C_{quat}$), 151.76 ($C_{quat}$), 156.23 (2 × $C_{quat}$), 182.73 ($C_{quat}$; C═O), 185.26 ($C_{quat}$; C═O). IR (ATR): $\tilde{\nu}$ = 2955 (m), 2927 (m), 2858 (m), 1661 (s), 1601 (s), 1563 (w), 1465 (m), 1360 (w), 1317 (s), 1282 (s), 1241 (w), 1183 (m), 1165 (m), 1097 (s), 1020 (s), 1006 (m), 903 (m), 738 (s), Ms (APCI) *m*/*z* (%): 1108 (100) [$M^+$].

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15 CCDC-827083 contains the supplementary crystallographic data for the structure **Q2**. See the Supporting Information.† C49H56O3 (692.94); crystal dimensions 0.30 × 0.48 × 0.60 $mm^3$, λ = 0.71073 Å, triclinic, $a$ = 9.466(2) Å, $b$ = 15.214(6) Å, $c$ = 16.716(5) Å, $\alpha$ = 64.80 (3)°, $\beta$ = 76.56 (2)°, $\gamma$ = 74.57 (2)°, $V$ = 2080.1 (11) $nm^3$, space group = $P\bar{1}$, Temp. = 293 (2) K, absorption coefficient = 0.067 $mm^{-1}$, $\theta$ range for data collection = 2.25–23.54°, reflections collected = 6447, reflections used in refinement = 6180, number of refined parameters = 465, absorption correction = none, refinement method = full matrix, $R$/$Rw$ values = 0.0806/0.2198, Goodness-of-fit ($F^2$) = 0.999, final shift = 0.0001, ($\Delta\rho$)min = 0.403 $eÅ^{-3}$, ($\Delta\rho$)max = −0.333 $eÅ^{-3}$

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