Synthesis of novel 2,5-diarylselenophenes from selenation of 1,4-diarylbutane-1,4-diones or methanol/arylacetylenes†

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Reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$ (Woollins' reagent, **WR**) with one equivalent of 1,4-diarylbutane-1,4-diones **1a–g** in refluxing toluene affords the corresponding 2,5-diarylselenophenes **2a–g** in excellent yields (up to 99%). Alternatively, the 2,5-diarylselenophenes (**2a** and **2b**) can be obtained in 70–80% yields from the reaction of arylacetylene with an equivalent of *O*-methyl *Se*-hydrogen phenylphosphonodiselenoate; the latter was derived from **WR** and methanol. The first X-ray structure of 2,5-diarylselenophenes is presented along with characterisation of their redox properties.

Introduction

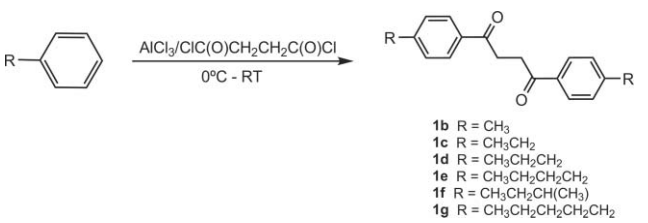
Selenophenes play an important role in the chemistry of organochalcogen compounds.[1–3] The first synthesis of selenophene was reported in 1885 by Paal, who obtained 2,5-dimethylselenophene by heating hexane-2,5-dione with phosphorus pentaselenide.[4] Since then, several selenium analogues of furans and thiophenes have been prepared by replacing the oxygen or the sulfur atom, respectively, in order to improve the bioactivity of these compounds. Some examples of the synthesis of selenophene and its 2,5-substituted derivatives include (1) the nucleophilic addition of hydrogen selenide or sodium selenide to diacetylenes[5–7] to give 2,5-diphenylselenophenes in low yield in the presence of Ag^+ or Cu^+; (2) the reaction of complicated reduced systems such as elemental selenium/$N_2H_4{\cdot}H_2O$/KOH/H_2O/DMSO, elemental selenium/$NaBH_4$/EtOH/DMF, elemental selenium/$NaBH_4$/KOH/H_2O/DMF or elemental selenium/$SnCl_2$/KOH/H_2O/DMSO with diphenyldiacetylene;[8] (3) the electrophilic cyclization of selenoenynes or the palladium-catalyzed Suzuki cross-coupling of 2-haloselenophenes,[9,10] and (4) the synthesis of 2,5-diarylselenophenes by thermolysis of 4-arylselenadiazoles with arylacetylenes. However, the latter method requires a large excess of arylacetylene (up to 10 equiv.) and has low selectivity (a mixture of three different symmetrical and unsymmetric selenophenes) and low yield.[11]

2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$, known as Woollins' reagent, **WR**, is a selenium counterpart of the well-known Lawesson's reagent, $[p\text{-}MeOC_6H_4P(S)(\mu\text{-}S)]_2$. Compared with other selenium reagents, **WR** has less unpleasant chemical properties, and is readily prepared and safely handled in air.[12] **WR** has been applied as a selenation agent for the synthesis of a wide range of selenoamides and selenoaldehydes by simple oxygen/selenium exchange or reaction with ArCN followed by hydrolysis as well as for the synthesis of a variety of P–Se heterocycles.[13–16] We have recently applied **WR** to the syntheses of symmetrical and unsymmetrical (*E*)-olefins from the corresponding ketones or aldehydes.[17] Furthermore, deoxygenation of sulfoxides with **WR** gives the corresponding sulfides under mild conditions.[18] As part of our interest in exploring the reactivity of **WR** towards different organic substrates, herein we report two efficient routes for the synthesis of new 2,5-diarylselenophenes by reaction of **WR** with 1,4-diarylbutane-1,4-diones or **WR**/methanol with arylacetylene under mild conditions. The first representative sample of the X-ray crystallographic structure of 2,5-diarylselenophenes and electrochemical properties were also investigated.

Results and discussion

Synthesis of 2,5-diarylselenophenes 2a–g

Preparation of 1,4-diarylbutane-1,4-diones **1b–g** was straightforward *via* one-pot Friedel–Crafts acylation from succinyl chloride with two equivalents of alkyl-substituted aromatics in the presence of anhydrous aluminium chloride at 0 °C to room temperature in high yields (Scheme 1). However, we were unable to synthesize analogues of 1,4-diarylbutane-1,4-diones with electron-withdrawing groups such as NO_2, $^+N(CH_3)_3$, COOH, C(O)R and CF_3, as



Scheme 1 The preparation of 1,4-diarylbutane-1,4-diones **1b–g** by Friedel–Crafts acylation.

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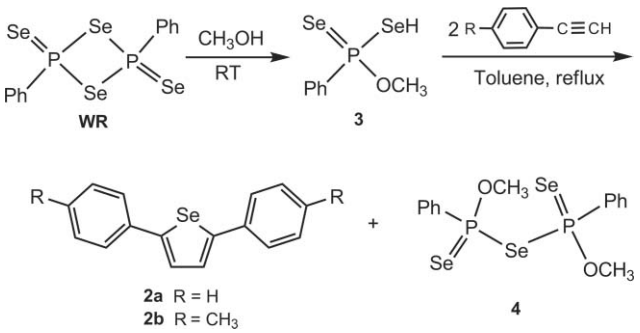
Friedel–Crafts acylation does not occur when these groups are on the aromatic ring.

Preparation of 2,5-diarylselenophenes **2a–g** were carried out by a typical procedure: an equimolar mixture of **WR** and 1,4-diarylbutane-1,4-dione was refluxed in toluene for 20 h. During this period, the red suspension gradually disappeared and the pale yellow solution was formed with precipitation of small amounts of grey elemental selenium. Upon cooling to room temperature the solution was passed through a silica gel column (toluene as eluent). The fractions containing the product were combined and concentrated in vacuum to give the air and moisture stable pale yellow solids of **2a–g** in excellent isolated yields (83–99%) (Scheme 2).

It is well known that **WR** is an efficient oxygen/selenium exchange reagent.[12–15] Mechanistically, we propose that the 1,4-dioxo groups are initially converted to 1,4-diselenones, a known replacement of carbonyl by selenone. The latter subsequently undergoes *in situ* cyclisation and elimination of H_2Se to give a more stable five-membered ring selenophene (Scheme 2). Formation of by-product $(PhPO_2)_3$ trimer was confirmed in the crude mixture by ^{31}P NMR.[18]

In an alternative approach, a methanolic suspension of **WR** was stirred at room temperature for 2 h, then at 50 °C for 1 h. The red suspension became a yellow solution accompanied by trace amount of grey precipitate of elemental selenium. After removal of the trace amount of selenium by filtration, the filtrate was evaporated in vacuum and the residue was dissolved in toluene. Equimolar amounts of phenylacetylene or 4-ethynyltoluene were added and the mixture was refluxed for 10 h. The mixture was cooled to room temperature and purified by silica gel chromatography (toluene as eluent) to give **2a** and **2b** in good yields (70 and 72% isolated yields, respectively) after recrystallization from dichloromethane–n-hexane. The use of excess of phenylacetylene or 4-ethynyltoluene (two or three equivalents) did not improve the yields of **2a** and **2b**. However, longer refluxing (up to 48 h) did enhance the yields of **2a** and **2b** to 75 and 80%.

The reaction pathway (Scheme 3) involves the generation of *O*-methyl *Se*-hydrogen phenylphosphonodiselenoate **3**, which reacts with phenylacetylene or 4-ethynyltoluene to afford the corresponding 2,5-diarylselenophenes **2a** and **2b** and byproduct **4**. The presence of byproduct **4** in the crude mixture was confirmed by ^{31}P and ^{77}Se NMR spectra [$\delta_P = 81.2$ ($J_{(P\text{-}Se)} = 460$ Hz, $J_{(P=Se)} = 822$ Hz) ppm and $\delta_{Se} = 221.3$ ($J_{(P\text{-}Se)} = 460$ Hz) and 95.5 ($J_{(P=Se)} = 822$ Hz) ppm].

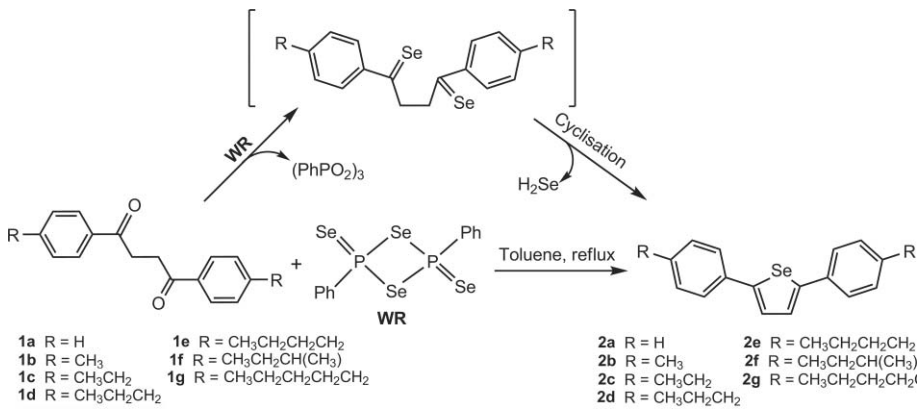


Scheme 3 Preparation of 2,5-diarylselenophenes **2a** and **2b** from phenylacetylene or 4-ethynyltoluene.

Although **2a** and **2b** are known compounds,[9–11] we have found no published ^{77}Se NMR and X-ray crystal structure data on 2,5-diarylselenophenes, and thus describe the first example here (Fig. 1). All compounds were ascertained by accurate mass measurement, IR, MS and solution multi-nuclear NMR spectroscopy. **2a–g** showed the anticipated $[M]^+$ peak in their mass spectra. Their accurate mass measurements were satisfactory. The ^{77}Se NMR spectra show single peaks in the range of 569.0–576.9 ppm for **2a–g**. These values are considerably lower than that of nonsubstituted selenophene (605 ppm),[19] but much higher than that of double fused ring selenophene (549 ppm).[20] Recrystallisation from chloromethane–n-hexane gave a colourless crystal of **2b**. The X-ray structure of **2b** shows the expected five membered (C–C–Se–C–C) ring skeleton. The bond lengths and angles in **2b** are as expected compared with other substituted selenophenes with the presence of relatively long Se–C bonds (*ca.* 1.92–1.94 Å expected for a single C–Se bond),[20–22] indicating that the extent of delocalisation is limited.

Electrochemical studies

CV's of **2a** and the nitrogen substituted analogue 2,5-diphenyl–3,4-diazaselenophene (**dpas**)[23] are shown in Fig. 2 and 3, respectively. **2a** shows two successive one-electron oxidation processes with peak oxidation potentials of +0.82 and +0.98 V *vs.* Fc/Fc^+ whilst the CV of **dpas** does not show a distinct oxidation peak,



Scheme 2 Preparation of 2,5-diarylselenophenes **2a–g** from the selenation of the corresponding 1,4-diarylbutane-1,4-diones **1a–g**.

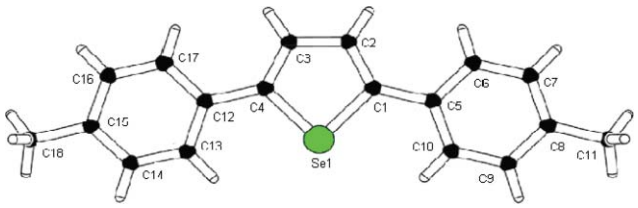


Fig. 1 X-Ray crystal structure of **2b**, selected bond lengths (Å) and angles (°) Se(1)–C(1) 1.877(3), C(3)–C(4) 1.365(5), Se(1)–C(4) 1.879(3), C(1)–C(5) 1.473(5), C(1)–C(2) 1.372(5), C(4)–C(11) 1.478(5), C(2)-C(3) 1.410(5), C(1)–Se(1)–C(4) 87.7(8), C(4)–C(3)–C(2) 116.1(3), C(2)–C(1)–Se(1) 110.2(2), C(3)–C(4)–Se(1) 110.2(3), C(3)–C(2)–C(1) 115.7(3).

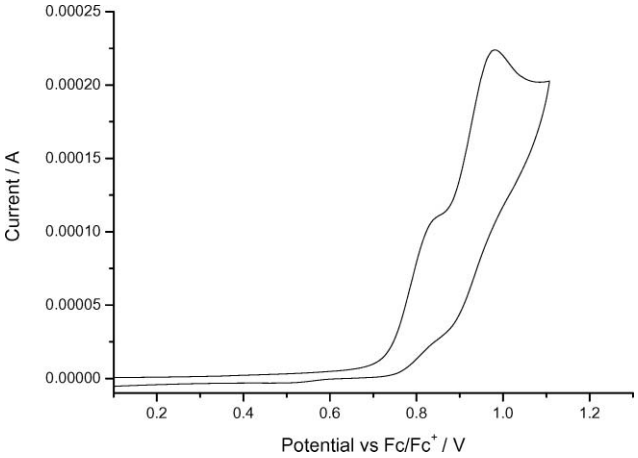


Fig. 2 CV of 2,5-diphenylselenophene (**2a**) (1 mM) in acetonitrile and background electrolyte. Sweep rate = 100 mV s^{-1}.

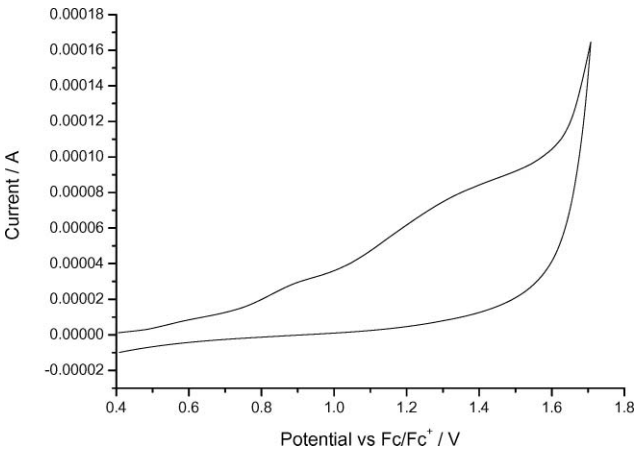


Fig. 3 CV of 2,5-diphenyl–3,4-diazaselenophene (**dpas**) (1.1 mM) in acetonitrile and background electrolyte. Sweep rate = 100 mV s^{-1}.

but shows a broad one electron oxidation feature between +1.4 and +1.6 V *vs.* Fc/Fc^+. The first oxidation of each species is chemically irreversible. This behavior is often seen for 5-membered heterocyclic systems such as pyrroles, thiophenes and furans; in these cases this is attributed to monomer radical cation coupling following oxidation to give (typically conducting) polymeric products.[24] Although CV cycling to potentials past the first oxidation peak gave a thin conducting layer from **2a**, successive cycling showed no evidence for progressive film growth in the 1–10 mM concentration range. Comparison of the fluorescence of this film, when dissolved in ethanol, showed no change compared with **2a**, with both exhibiting maximum peak excitation and emissions wavelengths of 326 and 370 nm respectively and a (0,0) transition at 348 nm. This suggests that the electrooxidation of **2a** yields an insoluble product which retains the fluorescence properties of **2a**. In contrast, upon electrooxidation, **dpas** formed a non-conducting layer of material (shown by the loss of electrode activity on successive CV cycling) on the electrode surface; both **dpas** and the formed film showed dramatically weaker fluorescence emission, with **dpas** peak excitation and emission wavelengths in ethanol at 279 and 345 nm, respectively, and a (0,0) transition around 315 nm.

The calculated peak oxidation potentials for the first one electron oxidations were +0.80 ± 0.03 V and +1.54 ± 0.03 V *vs.* Fc/Fc^+ for **2a** and **dpas**, respectively. These are in good agreement with that measured for **2a** and the centre of the broad oxidation peak observed for **dpas**. Fig. 4 shows the electron spin density maps for the resulting radical cations of both species; as expected, the regions of highest electron spin density (blue) show the largest change in electron density on oxidation and therefore are also the regions of most positive cationic charge density in the radical cation. It can be seen that for both diphenylselenophenes that the majority of the electron spin density is at the 2 and 5 positions of the central selenophene ring and not delocalised across the peripheral benzene rings. Given that the coupling of such heteroaromatic radical cations is thought to occur at peripheral sites of high electron spin density,[24] this predominantly central location of the electron spin density at sites inaccessible to coupling could explain the absence of extensive polymerisation on electrooxidation observed with other heteroaromatics.[25]

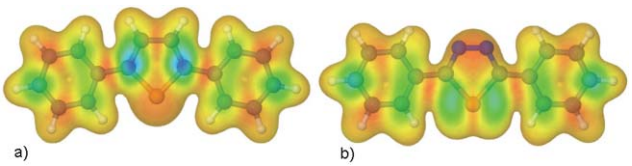


Fig. 4 Spin density distribution mapped onto a 99% electron density isosurface for the planar radical cations of (a) **2a** and (b) **dpas**. The colouring is schematic as follows: blue indicates a positive electron spin density (0.004) whilst red is negative (–0.001).

Conclusions

In summary, the synthesis of 2,5-diarylselenophenes **2a–g** has been carried out by direct selenation of 1,4-diarylbutane-1,4-diones by **WR**. The same diarylselenophenes can also be obtained from the reaction of arylacetylene and the methanolised intermediate of **WR**. Due to the limited availability of arylacetylene analogues, we only synthesised two examples; **2a** and **2b**. Representative **2a** shows significant redox, fluorescence and thin conducting film formation properties, which indicate that 2,5-diarylselenophene systems may be of interest for materials applications.

Experimental

1,4-Diphenylbutane-1,4-dione (**1a**) was purchased from Sigma-Aldrich. Other reagents or solvents, purchased from

Sigma-Aldrich or Alfa Aesar were used without further purification. Unless otherwise stated, all reactions were carried out under an oxygen-free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques; subsequent chromatographic and work up procedures were performed under aerobic conditions. ^{1}H (270 Hz), ^{13}C (67.9 Hz), ^{31}P (109 Hz) and ^{77}Se (51.4 Hz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea (U.K.) and the University of St Andrews Mass Spectrometry Service.

Electrochemistry

Electrochemical studies were carried out using a modular potentiostat/galvanostat with combined waveform generator and voltage sources (PGSTAT12, Autolab), with PC control, data collection and analysis carried out using the General Purpose Electrochemical System (GPES, Autolab) software. The working electrode was a platinum rotating disc electrode, RDE, (Oxford Electrodes Ltd.), disc area 0.387 cm^2. A 2 cm^2 platinum gauze was used as the counter electrode. The reference electrode (Bioanalytical Systems Inc.) consisted of a silver wire dipped in a 0.01 M solution of $AgClO_4$ in background electrolyte in a glass body with a VYCOR frit.

Electrochemical calculations: structures were calculated using the Gaussian 03 program[26]using uB3LYP/6-311+G(d,p), with acetonitrile solvation modeled with the SCRF method. It has previously been shown that accurate calculation of absolute values of experimental indole oxidation potentials is possible to within a few tens of millivolts, making this suitable as a reference redox reaction.[25c] Calculation of the free energy of the reaction 4+$^{\bullet}$ + In → 4 + In+$^{\bullet}$ gives the standard reduction potential of 4+$^{\bullet}$/4 relative to the indole (In) redox couple In+$^{\bullet}$/In. This can then be converted to a calculated peak oxidation potential on any reference scale by using the experimentally measured value of the indole peak oxidation potential, if reactants and products have similar diffusion coefficients in solution, which is usually a reasonable assumption for extended aromatics.[26c] The error limits quoted are those determined from comparison of the calculated and observed redox potentials of a range of redox-active aromatics.[25c]

The general procedure for the preparation of 1,4-diarylbutane-1,4-dione (1b–g)

Alkyl-substituted benzene (15 cm^3) and anhydrous aluminium chloride (5.0 g, 37 mmol) were placed in a three-necked flask fitted with a thermometer, a dropping funnel and a water condenser, while stirring under N_2 with a magnetic stirrer. The mixture was cooled to 0 °C and succinyl chloride (2.7 g, 18.5 mmol) was added dropwise within 30 min. The ice bath was removed and the mixture was allowed to stir at room temperature for one hour. Then, the mixture was poured slowly onto a stirring solution of concentrated hydrochloric acid (10%, 20 cm^3). The contents were transferred to a separation funnel with the help of diethyl ether (30 cm^3). The diethyl ether–toluene and diethyl ether extracts were washed with water (30 cm^3 × 3) and brine (30 cm^3). The combined extracts were dried over K_2CO_3 (2.0 g) overnight and filtered. The filtrate was evaporated *in vacuo*. The residue was dissolved in dichloromethane and purified by column chromatography (silica gel, 1 : 9 ethyl acetate–dichloromethane as eluent) to give the expected products **1b–g**.

1,4-Di-*p*-tolylbutane-1,4-dione (1b). 4.53 g as a white solid in 92% yield. Selected IR (KBr, cm^{-1}): 2963(m), 2929(w), 1680(s), 1602(s), 1565(m), 1399(m), 1358(m), 1230(s), 1170(m), 832(s), 557(s). ^{1}H NMR ($CDCl_3$, δ), 7.92 (d, J(H,H) = 8.4 Hz, 4H, ArH), 7.25 (d, J(H,H) = 8.4 Hz, 4H, ArH), 3.41 (s, 4H, CH_2), 2.29 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 198.5 (C=O), 144.0, 134.4, 129.4, 128.2, 32.6, 21.7 ppm. MS (ES$^+$, m/z): 289 [M + Na]$^+$. Anal. calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.49; H, 7.00.

1,4-Bis(4-ethylphenyl)butane-1,4-dione (1c). 5.05 g as a white solid in 93% yield. Selected IR (KBr, cm^{-1}): 2965(m), 2931(w), 1680(s), 1604(s), 1565(m), 1397(m), 1358(m), 1228(s), 1170(m), 993(s), 832(s), 558(s), 497(m). ^{1}H NMR (CD_2Cl_2, δ), 7.97 (d, J(H,H) = 7.7 Hz, 4H, ArH), 7.32 (d, J(H,H) = 7.7 Hz, 4H, ArH), 3.40 (s, 4H, CH_2), 2.72 (q, J(H,H) = 7.4 Hz, 4H, CH_2), 1.28 (t, J(H,H) = 7.4 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 198.2 (C=O), 150.2, 134.8, 129.3, 128.1, 32.5, 29.0, 15.2 ppm. MS (ES$^+$, m/z): 317 [M + Na]$^+$. Anal. calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.30; H, 7.85.

1,4-Bis(4-propylphenyl)butane-1,4-dione (1d). 5.20 g as a white solid in 88% yield. Selected IR (KBr, cm^{-1}): 2955(m), 2868(w), 1675(s), 1604(s), 1315(m), 1174(s), 1002(s), 785(s). ^{1}H NMR (CD_2Cl_2, δ), 7.95 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.30 (d, J(H,H) = 8.3 Hz, 4H, ArH), 3.40 (s, 4H, CH_2), 2.66 (t, J(H,H) = 7.5 Hz, 4H, CH_2), 1.75-1.61 (m, 4H, CH_2), 0.96 (t, J(H,H) = 7.5 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 198.2 (C=O), 148.6, 134.8, 128.7, 128.2, 38.0, 32.5, 24.4, 13.7 ppm. MS (ES$^+$, m/z): 345 [M + Na]$^+$. Anal. calcd. for $C_{22}H_{26}O_2$: C, 81.95; H, 8.12. Found: C, 82.20; H, 8.32.

1,4-Bis(4-butylphenyl)butane-1,4-dione (1e). 5.61 g as a white solid in 87% yield. Selected IR (KBr, cm^{-1}): 2956(m), 2859(w), 1673(s), 1605(s), 1324(m), 1178(s), 1006(s), 787(m). ^{1}H NMR (CD_2Cl_2, δ), 7.95 (d, J(H,H) = 8.0 Hz, 4H, ArH), 7.31 (d, J(H,H) = 8.0 Hz, 4H, ArH), 3.40 (s, 4H, CH_2), 2.66 (t, J(H,H) = 7.4 Hz, 4H, CH_2), 1.66-1.58 (m, 4H, CH_2), 1.42-1.33 (m, 4H, CH_2), 0.95 (t, J(H,H) = 7.4 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 198.2 (C=O), 148.9, 134.7, 128.7, 128.2, 35.7, 33.4, 32.5, 22.4, 13.8 ppm. MS (ES$^+$, m/z): 373 [M + Na]$^+$. Anal. calcd. for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.66; H, 8.52.

1,4-Bis(4-*sec*-butylphenyl)butane-1,4-dione (1f). 5.50 g as a white solid in 85% yield. Selected IR (KBr, cm^{-1}): 2963(m), 2920(w), 1675(s), 1604(s), 1362(m), 1228(s), 1181(m), 992(s), 835(s), 570(s). ^{1}H NMR (CD_2Cl_2, δ), 7.96 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.30 (d, J(H,H) = 8.3 Hz, 4H, ArH), 3.40 (s, 4H, CH_2), 2.75-2.62 (m, 2H, CH), 1.68-1.60 (m, 4H, CH_2), 1.25 (d, J(H,H) = 6.9 Hz, 6H, CH_3), 0.82 (t, J(H,H) = 6.9 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 198.3 (C=O), 153.6, 134.9, 128.2, 127.8, 41.9, 32.5, 31.0, 21.4, 12.0 ppm. MS (ES$^+$, m/z): 373 [M + Na]$^+$. Anal. calcd. for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63; Found: C, 82.14; H, 9.15.

1,4-Bis(4-pentylphenyl)butane-1,4-dione (1g). 5.20 g as a white solid in 75% yield. Selected IR (KBr, cm^{-1}): 2922(m), 2857(w), 1671(s), 1604(s), 1411(s), 1324(s), 1177(s), 1006(s), 786(s), 561(m), 524(m). ^1H NMR (CD_2Cl_2, δ), 7.95 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.30 (d, J(H,H) = 8.3 Hz, 4H, ArH), 3.40 (s, 4H, CH_2), 2.68 (t, J(H,H) = 8.0 Hz, 4H, CH_2), 1.71-1.62 (m, 4H, CH_2), 1.37-1.34 (m, 8H, CH_2), 0.92 (t, J(H,H) = 8.0 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 198.2 (C=O), 148.9, 134.7, 128.7, 128.2, 36.0, 32.5, 31.6, 30.9, 22.6, 13.9 ppm. MS (ES^+, m/z): 401 $[M + Na]^+$. Anal. calcd. for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05. Found: C, 82.59; H, 9.43.

The general procedure for the synthesis of 2,5-diarylselenophenes (2a–g) from the selenation of 1,4-diarylbutane-1,4-dione

1,4-Diarylbutane-1,4-dione (1.0 mmol) and **WR** (1.0 mmol) in dry toluene (10 cm^3) was refluxed for 20 h. The red suspension gradually disappeared and a pale yellow solution formed along with small amount of elemental selenium precipitate. Upon cooling to room temperature the mixture was purified by silica gel column chromatography (toluene as eluent). The fractions containing the product were combined and the solvent was removed *in vacuo* to give the target product **2a–g**.

The synthesis of 2,5-diarylselenophenes 2a and 2b from the reaction of WR/methanol with arylacetylene

A red suspension of **WR** (1.0 mmol) in methanol (20 cm^3) was stirred at room temperature for 2 h, then at 50 °C for 1 h. During this period the red suspension gradually disappeared and a yellow solution formed along with trace amount of elemental selenium precipitate. The mixture was filtered to remove the trace amount of elemental selenium and the filtrate was evaporated in vacuum to give *O*-methyl *Se*-hydrogen phenylphosphonodiselenoate (**3**) as a white solid in 99% yield. To the solution of **3** in dry toluene (10 cm^3), phenylacetylene or 4-ethynyltoluene (2.0 mmol) was added and the mixture was refluxed for 20 h. The mixture was cooled to room temperature and purified by column chromatography (silica gel, toluene as eluent) to afford **2a** and **2b**.

2,5-Diphenylselenophene (2a). Pale yellow solid, 280 mg (99% yield) from the selenation of 1,4-diphenylbutane-1,4-dione; 199 mg (70% yield) from the reaction of **WR**/methanol with phenylacetylene. IR (KBr, cm^{-1}), 1480 (m), 1460(m), 1447(m), 1262(m), 1024(m), 796(m), 756(s), 690(s), 672(m). ^1H NMR ($CDCl_3$, δ), 7.76 (d, J(H,H) = 7.4 Hz, 2H, CH=CH), 7.58 (d, J(H,H) = 7.2 Hz, 4H, ArH), 7.40 (m, J(H,H) = 7.2 Hz, 4H, ArH), 7.29 (m, J(H,H) = 7.2 Hz, 2H, ArH) ppm. ^{13}C NMR ($CDCl_3$, δ), 150.0, 136.5, 129.0, 127.7, 127.4, 126.2, 126.1 ppm. ^{77}Se NMR ($CDCl_3$, δ), 576.9 ppm. MS (EI^+, m/z): 284 $[M]^+$. Accurate mass measurement (EIMS): 284.0104, calculated mass for $C_{16}H_{12}Se$: 284.0109.

2,5-Di-*p*-toluoylselenophene (2b). Greenish yellow solid, 307 mg (99% yield) from the selenation of 1,4-di-*p*-toluoylbutane-1,4-dione; 225 mg (72% yield) from the reaction of **WR**/methanol with 4-ethynyltoluene. IR (KBr, cm^{-1}), 1503 (m), 1461 (w), 1122 (w), 1021 (w), 821 (m), 797 (vs), 541 (w), 498 (m), 449 (m). ^1H NMR ($CDCl_3$, δ), 7.63 (d, J(H,H) = 7.9 Hz, 2H, CH=CH), 7.44 (d, J(H,H) = 7.9 Hz, 4H, ArH), 7.17 (d, J(H,H) = 7.9 Hz, 4H, ArH), 2.28 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 149.7, 136.5, 133.8, 129.4, 126.0, 125.7, 123.7, 21.3 ppm. ^{77}Se NMR ($CDCl_3$, δ), 573.3 ppm. MS (EI^+, m/z): 312 $[M]^+$. Accurate mass measurement (EIMS): 312.0417, calculated mass for $C_{18}H_{16}Se$: 312.0421.

2,5-Bis(4-ethylphenyl)selenophene (2c). Pale yellow solid (330 mg, 97% yield). IR (KBr, cm^{-1}), 1503(m), 1460(m), 1121(m), 1022(m), 830(s), 790(s). ^1H NMR (CD_2Cl_2, δ), 7.67 (d, J(H,H) = 8.0 Hz, 2H, CH=CH), 7.41 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.23 (d, J(H,H) = 8.3 Hz, 4H, ArH), 2.66 (q, J(H,H) = 7.4 Hz, 4H, CH_2), 1.25 (t, J(H,H) = 7.4 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 153.3, 149.3, 142.1, 128.5, 125.9, 123.6, 28.7, 15.5 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 569.4 ppm. MS (EI^+, m/z): 340 $[M]^+$. Accurate mass measurement (EIMS): 336.0752, calculated mass for $C_{20}H_{20}{}^{76}Se$: 336.0774.

2,5-Bis(4-propylphenyl)selenophene (2d). Pale yellow paste (332 mg, 90% yield). IR (KBr, cm^{-1}), 1503(m), 1462(m), 1022(m), 790(s). ^1H NMR (CD_2Cl_2, δ), 7.67 (d, J(H,H) = 8.0 Hz, 2H, CH=CH), 7.49 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.23 (m, J(H,H) = 8.3 Hz, 4H, ArH), 2.60 (t, J(H,H) = 8.0 Hz, 4H, CH_2), 1.71-1.63 (m, 4H, CH_2), 0.97 (t, J(H,H) = 8.0 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 153.3, 142.2, 133.8, 128.9, 125.7, 123.6, 37.7, 24.7, 13.7 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 569.1 ppm. MS (EI^+, m/z): 368 $[M]^+$, 304 $[M - C_4H_{16}]^+$, 275 $[M - C_4H_{16} - C_2H_5]^+$. Accurate mass measurement (EIMS): 364.0902, calculated mass for $C_{22}H_{24}{}^{76}Se$: 364.1062.

2,5-Bis(4-butylphenyl)selenophene (2e). Pale yellow paste (350 mg, 83% yield). IR (KBr, cm^{-1}), 1503(m), 1462(m), 1022(m), 831(m), 780(s). ^1H NMR (CD_2Cl_2, δ), 7.68 (d, J(H,H) = 8.0 Hz, 2H, CH=CH), 7.50 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.23 (m, J(H,H) = 8.3 Hz, 4H, ArH), 2.65 (t, J(H,H) = 8.0 Hz, 4H, CH_2), 1.71-1.62 (m, 4H, CH_2), 1.47-1.34 (m, 4H, CH_2), 0.97 (t, J(H,H) = 8.0 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 153.3, 142.7, 133.8, 129.0, 125.8, 123.6, 35.5, 33.7, 22.5, 13.9 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 569.1 ppm. MS (EI^+, m/z): 396 $[M]^+$, 332 $[M - C_4H_{16}]^+$, 289 $[M - C_4H_{16} - C_3H_7]^+$. Accurate mass measurement (EIMS): 392.1377, calculated mass for $C_{24}H_{28}{}^{76}Se$: 392.1375.

2,5-Bis(4-*sec*-butylphenyl)selenophene (2f). Pale yellow paste (390 mg, 98% yield). IR (KBr, cm^{-1}), 1503(m), 1462(m), 1022(m), 790(s). ^1H NMR (CD_2Cl_2, δ), 7.67 (d, J(H,H) = 8.0 Hz, 2H, CH=CH), 7.49 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.23 (m, J(H,H) = 8.3 Hz, 4H, ArH), 2.64 (d, J(H,H) = 7.2 Hz, 6H, CH_3), 1.64-1.52 (m, 2H, CH), 1.26-1.23 (m, 4H, CH_2), 0.97 (t, J(H,H) = 7.2 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 153.3, 147.5, 134.0, 127.7, 125.8, 123.6, 41.5, 31.1, 21.6, 12.1 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 569.1 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 569.2 ppm. MS (EI^+, m/z): 396 $[M]^+$. Accurate mass measurement (EIMS): 396.1356, calculated mass for $C_{24}H_{28}Se$: 396.1357.

2,5-Bis(4-pentylphenyl)selenophene (2g). Pale yellow paste (360 mg, 85% yield). IR (KBr, cm^{-1}), 1503(m), 1462(m), 1122(m), 1025(m), 832(m), 793(s). ^1H NMR (CD_2Cl_2, δ), 7.66 (d, J(H,H) = 8.3 Hz, 2H, CH=CH), 7.49 (d, J(H,H) = 8.3 Hz, 4H, ArH), 7.24 (m, J(H,H) = 8.3 Hz, 4H, ArH), 2.63 (t, J(H,H) = 7.5 Hz, 4H, CH_2), 1.66-1.61 (m, 4H, CH_2), 1.37-1.33 (m, 8H, CH_2), 0.92 (t, J(H,H) = 7.5 Hz, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 153.3, 149.3, 142.5, 128.8, 125.8, 123.6, 35.7, 31.6, 31.2, 22.6, 13.9 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 569.0 ppm. MS (EI^+, m/z): 424 $[M]^+$. Accurate mass measurement (EIMS): 420.1691, calculated mass for $C_{26}H_{32}{}^{76}Se$: 420.1714.

***O*-Methyl Se-hydrogen phenylphosphonodiselenoate (3).** ^{1}H NMR (CD_2Cl_2, δ), 7.92 (m, 2H, ArH), 7.49 (m, 1H, ArH), 7.33 (m, 2H, ArH), 3.78 (d, ^{3}J(P,C) = 16.1 Hz, 3H, OCH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 131.4 (d, ^{1}J(P,C) = 98.6 Hz), 130.3 (d, ^{3}J(P,C) = 11.4 Hz), 128.5 (d, ^{2}J(P,C) = 31.1 Hz), 128.4, 53.5 (d, (d, ^{2}J(P,C) = 54.0 Hz) ppm. ^{31}P NMR (CD_2Cl_2, δ), 84.31 (s, J(P–Se) = 441 Hz, J(P=Se) = 831 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 241.41 (d, J(P–Se) = 441 Hz), -111.52 (d, J(P–Se) = 831 Hz) ppm. MS (ESI^{+}, m/z): 321 [M + Na].

Crystallographic data for 2b. $C_{18}H_{16}Se$, M = 311.27, orthorhombic, space group *Pbca*, a = 14.556(2), b = 5.8313(9), c = 33.051(5) Å, U = 2805.4(8) Å^3, Z = 8, D_c = 1.474 Mg m^{-3}, μ = 2.660 mm^{-1}, 16 322 reflections, 3107 unique (R_{int} = 0.0688); R_1 = 0.0560, wR_2 = 0.1337. X-Ray crystal data were collected at 93 K by using a Rigaku MM007 high brilliance RA generator/confocal optics and Mercury CCD system. Intensities were corrected for Lorentz-polarisation and for absorption. The structure was solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were obtained with full-matrix least-squares based on F^2 by using the program SHELXTL.[27] CCDC 657441 contains the supplementary crystallographic data for this paper. These data are available in the ESI.†

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