The syntheses, structures and spectroelectrochemical properties of 6-oxo-verdazyl derivatives bearing surface anchoring groups

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Abstract

A series of 6-oxo verdazyl radicals functionalised at the 1- and 5-positions by methyl, thiomethyl and iodo groups were synthesised using conventional strategies. Facile Sonogashira cross-coupling reactions of terminal alkynes with the diiodo analogue were used for synthetic elaboration of the verdazyl core structure with π -conjugated ethynyl groups. The radicals were characterised by EPR spectroscopy, single-crystal X-ray diffraction, cyclic voltammetry and optical spectroscopy. The chemically and electrochemically reversible oxidation and reduction of these radicals within a convenient redox window permitted further studies on the closed-shell cationic and anionic forms using spectroelectrochemical methods, supported by (TD-)DFT calculations.

Introduction

Derivatives of verdazyl (Figure 1a) and 6-oxoverdazyl (Figure 1b) are rare examples of charge neutral, air- and moisture-stable radicals.¹ The contemporary interest in verdazyl chemistry stems from the ready functionalisation of the 3-position (R^3 , Figure 1a,b) to create radical ligands, including chelating and pincer type structures, for use as spin labels.²⁻¹⁰ In addition verdazyl-based compounds have been used in the design of a variety of organic magnetic¹¹ and conductive materials.¹² These potential applications have prompted renewed interest in the synthetic chemistry associated with verdazyl-based structures,^{13, 14} including demonstrations of Sonogashira cross-coupling reactions that have used to extend the conjugation of an aryl groups either the 1- or 3-positions.^{15, 16}

Figure 1. Sketches of the generic structures of: (a) verdazyl compounds; (b) 6-oxoverdazyl compounds.

More generally, radical molecular species have been identified as exceptionally promising compounds for use in the development of the field of molecular electronics.¹⁷⁻²² The incorporation of a molecular system featuring an unpaired electron within an electrode | molecule | electrode junction leads to a host of fascinating electronic properties,²³ including enhanced rectification,²⁴ spin-gating,²⁵ Kondo effects,²⁶ magnetoresistive effects²⁷ and quantum interference,²⁸ whilst the redox-activity of such systems allows for an exciting range of electrochemically gated

applications.²⁹⁻³² This has prompted exploration of a small number of perchlorotriphenylmethyl radicals^{24, 33-36} as well as radical species generated within a molecular junction by in situ redox³⁷⁻⁴³ or chemical²⁸ processes.

A combination of these interests has prompted consideration of the potential for stable verdazyl-style radicals linked through the 1- and 5-positions to suitable anchor groups with a view to future incorporation within a molecular junction. Here we describe synthetic efforts in this direction, together with characterisation of the resulting radicals by EPR spectroscopy and representative crystallographically determined molecular structures. The facile single-electron oxidation and reduction processes that typify the verdazyl motif permit further exploration of the resulting closed shell redox products by spectroelectrochemical methods, supported by quantum chemical calculations.

Results and Discussion

The 1,5-disubstituted 6-oxo-verdazyl derivatives **4a – c** were prepared from 4-iodoaniline, 4-thiomethylaniline and 4-toluidine, respectively, using methods entirely analogous to those established in the literature (Scheme 1).^{1, 44} Each substituted aniline was initially converted to the hydrazine ArNHNH₂, and then reacted with benzaldehyde to install the phenyl ring that will ultimately occupy the 3-position in the final verdazyl products and give compounds **1a – c**. Subsequent treatment with triphosgene gave the hydrazinecarbonyl chlorides **2a – c**. The molecular structure of **2a** was determined by single-crystal X-ray diffraction (Figure S1, Table S1). The compounds **2a – c** were ring closed through further reaction with another equivalent of

the hydrazine affording the tetrazines **3a – c**. Oxidation (NaIO_4) of the tetrazines in turn gave the deeply coloured 6-oxo-verdazyl derivatives **4a – c** (Figure 2).

Scheme 1. Synthetic routes to tetrazines **3a – c** and 6-oxo-verdazyl radicals **4a – c**.

Reagents and conditions: (i) NaNO_2 , SnCl_2 , HCl ; (ii) PhCHO , EtOH ; (iii) Triphosgene, pyridine, EtOAc , MePh ; (iv) $4\text{-RC}_6\text{H}_4\text{NHNH}_2$, EtOH ; (v) NaIO_4 , CH_2Cl_2 , MeOH .

Figure 2. A photograph of solutions (*ca.* 0.25 mM in CH_2Cl_2) of the 6-oxo-verdazyl derivatives **4a – c**, **8**, **9** and **10** illustrating the variations in colour with the nature of the 1,5-substituents.

Sonogashira cross-coupling reactions were explored for the extension of the 6-oxo-verdazyl structures, initially from the iodo-functionalised tetrazine **3c** with the terminal acetylenes 4-ethynyl-aniline, 5-ethynyl-3,3-dimethyl-2,3-dihydrobenzo[*b*]thiophene and 4-ethynyl thioanisole (Scheme 2). These alkynes were chosen as coupling partners in order to introduce functionalities well known to serve as effective anchor groups to gold electrodes.⁴⁷⁻⁵² However, whilst the iodo-tetrazine **3c** underwent efficient Sonogashira cross-coupling reactions, affording the substituted tetrazines **5**, **6** and **7** in good to excellent yield, these extended derivatives were poorly soluble in most common solvents, making the subsequent oxidation reactions to give the verdazyls **8**, **9** and **10** sluggish and difficult to control. In addition, attempts to oxidise tetrazine **7** was further complicated by oxidation of the aniline-like substituent.

Alternatively, the iodo-verdazyl compound **4c** underwent Sonogashira cross-coupling reactions with each of 4-ethynyl-thioanisole, 5-ethynyl-3,3-dimethyl-2,3-dihydrobenzo[*b*]thiophene and 4-ethynyl-aniline without difficulty, giving the extended, intensely dark-green coloured ‘wire-like’ verdazyl compounds **8**, **9** and **10** directly and in high isolated yield after chromatographic work-up (Scheme 2, Figure 2). These latter reactions represent rare examples of the direct modification of the verdazyl sub-structure by cross-coupling reactions,¹⁶ and we believe compounds **8**, **9** and **10** to be the first examples of verdazyl derivatives with ethynyl moieties conjugated to both 1- and 5-positions.

The small molecule intermediates and tetrazines were readily characterised by the usual suite of ¹H and ¹³C{¹H} NMR spectroscopies, IR spectroscopy and mass spectrometry. The NMR spectra of the verdazyl compounds were significantly

paramagnetically broadened and shifted, making confident structural assignment difficult. However, the $\nu(\text{C}=\text{O})$ band was diagnostic over the course of the oxidation reactions of the tetrazines, shifting from 1620 – 1628 cm^{-1} in **3a – c** to higher frequencies in the 6-oxo-verdazyl radicals **4a – c**. The π -donor character of the iodo group is apparent in the 6-oxo-verdazyls, with the $\nu(\text{C}=\text{O})$ band in **4c** falling at 1688 cm^{-1} , compared with the bands at 1702 (**4a**) and 1697 (**4b**) cm^{-1} in the other examples. Similarly, in the alkynyl substituted tetrazine and 6-oxoverdazyl derivatives the $\nu(\text{C}=\text{O})$ bands fall in the range 1618 – 1636 cm^{-1} (**5 – 7**) and 1690 – 1698 cm^{-1} (**8 – 10**). The alkynyl $\nu(\text{C}\equiv\text{C})$ bands were found to be largely insensitive to the nature of the heterocyclic core or the substituent, and observed as weak, broad features over the narrow range of 2111 – 2117 cm^{-1} (**5 – 10**). The tetrazines **3a – c** and 6-oxoverdazyl radicals **4a – c** were further characterised by single-crystal X-ray diffraction, the longer examples **8**, **9** and **10** proving stubbornly resistant to crystallisation, by UV-vis-NIR spectroscopy, with assignments aided by TD-DFT calculations on model system, and by EPR spectroscopy.

Single-crystal X-ray structures

Single crystals of the tetrazines **3a** (Figure S2), **3b** (Figure 3) and **3c** (Figure S3) were obtained by the slow evaporation of solvents from concentrated solutions of the compounds in CD_2Cl_2 (**3a**) or CDCl_3 (**3b**, **c**). Crystals of the 6-oxo-verdazyls **4a** (Figure S4), **4b** (Figure 4) and **4c** (Figure S5) were also obtained by slow evaporation of concentrated solutions in toluene (**4a**, **b**) or dichloromethane (**4c**). Key metric and refinement parameters are summarised in Table 1 and Table S1, with further labeling given in Scheme 3.

Figure 3. A plot of the crystallographically determined molecular structure of **3b** with thermal ellipsoids of non-hydrogen atoms drawn at 50% probability; only selected H-atoms are shown for clarity.

Figure 4. A plot of the crystallographically determined molecular structure of **4b** with thermal ellipsoids at 50% probability; H-atoms are omitted for clarity.

All compounds present a full molecule per asymmetric unit with the exception of the tetrazines **3a** and **3c** which contain half and two molecule(s) per asymmetric unit, respectively. The other half of tetrazine **3a** is generated by a mirror plane through the O1,C1,C2,C3,C6 atoms. In all tetrazines **3a** – **c**, the crystallographically labeled C2 atoms sit 0.650(2), 0.662(4) and 0.63(3)/0.64(3) Å out of the mean plane through the

four N atoms of the tetrazine for **3a**, **3b** and **3c**, respectively, whilst C1 is displaced on the same side of the ring by 0.176(2), 0.147(3) and 0.06(3)/0.11(3) Å. This distorted boat-like conformation of the 6-membered C₂N₄ ring is characteristic of the tetrazine compounds while their verdazyl analogues display a planar central ring. This feature is illustrated by way of example for **3b** and **4b** (Figure 5) where the angle between the planes P_{N2,C2,N3} and P_{N1,N2,N3,N4} in **3b** (126.5(4)°) is compared with that in **4b**, (179.6(2)).

Figure 5. Lateral view of **3b** (left) and **4b** (right) highlighting the geometry changes of the tetrazine (**3b**) vs. verdazyl (**4b**) central ring, represented by plane intersections between P_{N2,C2,N3} and P_{N1,N2,N3,N4}.

For the tetrazine compounds, the N–N and N–C distances in the C₂N₄ core are consistent with the typical values for single bonds involving these elements, and the amide-like N–C bonds (**3a** N1 – C7; **3b**, **3c** N1–C9 and N4–C15) are also consistent with bonds of this type, confirming the suitability of the valence bond description (Scheme 1, Table 1). The N–N distances in the verdazyl rings fall in a narrow range 1.373(2) / 1.371(2) (**4a**), 1.373(3) – 1.375(3) Å (**4b**) and 1.361(6) / 1.365(6) Å (**4c**),

significantly shorter than in the **3a – c** analogues, but longer than typical N=N double bonds (ca. 1.25 Å). The amide-like N-C bond lengths (N1–C9 and N4–C15) are in the usual range and consistent with those in **3a – c**, whilst the shorter N–C bonds of the central C₂N₄ ring reflect a greater degree of delocalisation in the verdazyl radicals **4a – c** (Table 1). As with the tetrazines, there are no statistically significant variations in the bond lengths within the heterocyclic core as a function of the substituents (R = Me (**4a**), SMe (**4b**), I (**4c**)) (Table 1).

Table 1. Selected bond lengths (Å) and angles (°) from crystallographically determined structures of **3a**, **3b**, **3c**, **4a**, **4b** and **4c**

	3a R = Me	3b R = SMe	3c^b R = I	4a R = Me	4b R = SMe	4c R = I
Distances (Å)						
C1–N1	1.378(2)	1.386(4)	1.37(3) / 1.43(4)	1.388(2)	1.385(3)	1.404(7)
C1–N4	n/a	1.378(4)	1.39(3) / 1.34(3)	1.387(2)	1.393(3)	1.388(7)
N1–N2	1.432(2)	1.423(4)	1.46(3) / 1.43(3)	1.373(2)	1.373(3)	1.361(6)
N3–N4	n/a	1.431(4)	1.45(3) / 1.43(3)	1.371(2)	1.375(3)	1.365(6)
C2–N2	1.458(2)	1.463(4)	1.45(4) / 1.44(3)	1.330(2)	1.327(3)	1.331(6)
C2–N3	n/a	1.451(5)	1.43(4) / 1.48(4)	1.328(2)	1.324(3)	1.343(7)
C2–C3	1.520(3)	1.508(5)	1.50(4) / 1.48(4)	1.484(2)	1.386(3)	1.485(7)
N1–C9 ^a	1.431(2)	1.438(4)	1.46(4) / 1.43(4)	1.434(2)	1.432(3)	1.441(6)
N4–C15	n/a	1.433(4)	1.46(4) / 1.48(3)	1.436(2)	1.433(3)	1.435(7)
C1=O1	1.237(2)	1.227(4)	1.21(3) / 1.20(3)	1.215(2)	1.220(3)	1.204(6)
Plane intersections with the C₂N₄ core (°)						
α^c	31.40(6)	37.3(3)	47(1) / 48(1)	37.65(4)	42.4(1)	42.4(1)
β^d	n/a	34.8(3)	44(1) / 47(1)	42.84(5)	39.2(1)	39.2(1)
γ^e	8.2 (1)	11.7(4)	2(1) / 4(1)	10.54(6)	13.7(1)	3.3(1)

^a N1–C7 in **3a** and **B**, due to the mirror plane through the atoms O1,C1,C2,C3,C6.^b two values for **3c** reflecting the presence of two molecules in the asymmetric units.^{c, d, e} see Scheme 3.

Scheme 3. Rings and angles notation used in the structural description of the compounds reported herein.

UV-vis spectroscopy

The UV-vis-NIR spectra of the tetrazine derivatives **3a** – **c** each give contain an absorption feature near 35000 cm^{-1} (Figure 6, Figure S6). TD-DFT calculations (B3LYP / 6-31G*(df,p)/COSMO(CH₂Cl₂)) carried out on the model system 2,4,6-triphenyl-1,2,4,5-tetrazinan-3-one (**A**) (Figure 6, Table S2) assign these bands to the HOMO-LUMO transitions (calculated for **A** at $\tilde{\nu} = 34691\text{ cm}^{-1}$; $f = 0.3636$), which have charge transfer character from the tetrazine core to the peripheral phenyl rings X, Y and especially Z (Scheme 3, Table S2). The introduction of the ethynyl moiety in **5**, **6** and **7** results in a red-shift in the absorption envelope to *ca.* $30,000\text{ cm}^{-1}$ with a degree of additional fine structure evident (Figure S6).

Figure 6. The UV-vis spectra ($\tilde{\nu}_{max} / \text{cm}^{-1}$ ($\epsilon / \text{M}^{-1}\text{cm}^{-1}$)) of the representative tetrazine **3a**, together with a sketch of the model tetrazine **A**, and plots of key molecular orbitals of **A** against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH_2Cl_2)). Contours plotted at $\pm 0.002 (\text{e}/\text{bohr}^3)^{1/2}$.

The UV-vis spectra of the corresponding 6-oxo-verdazyl radicals **4a – c** each give rise to at least four absorption features: a band at *ca.* 17000 cm^{-1} , a collection of weak bands near 25000 cm^{-1} , a strong envelope at 28000 cm^{-1} and very intense high energy transitions above 38000 cm^{-1} (Figure 7, Figure S7). TD-DFT calculations on the model compound 1,3,5-triphenyl-6-oxoverdazyl (**B**) (Figure 7, Table S3) allow all transitions to be assigned. The low energy absorptions near *ca.* 17000 cm^{-1} responsible for the 6-oxo-verdazyl intense colour in the experimental systems are assigned to the β -HOMO – β -LUMO transitions from the model **B** ($\tilde{\nu} = 18937 \text{ cm}^{-1}$, $f = 0.0495$), which results in

charge transfer from the Z ring to the verdazyl core (Table S3). The absorptions near 25000 cm^{-1} are assigned to the $[\beta\text{-HOMO}-1] - \beta\text{-LUMO}$ ($\tilde{\nu} = 21606\text{ cm}^{-1}$, $f = 0.0076$) and $\alpha\text{-HOMO} - \alpha\text{-LUMO}$ ($\tilde{\nu} = 23099\text{ cm}^{-1}$, $f = 0.0166$) transitions which re-distribute charge from the peripheral rings to the heterocyclic core and phenyl ring (Z). The 28000 cm^{-1} envelope is attributed to charge transfer from the heterocyclic core to the π^* systems of the X and Y phenyl rings ($\alpha\text{-HOMO} - \alpha\text{-[LUMO+1]}$) ($\tilde{\nu} = 29148\text{ cm}^{-1}$, $f = 0.1831$) and the intense, high energy transition above $38,000\text{ cm}^{-1}$ as two $\pi\text{-}\pi^*$ transitions ($\tilde{\nu} = 36751\text{ cm}^{-1}$, $f = 0.2493$ and $\tilde{\nu} = 37219\text{ cm}^{-1}$, $f = 0.2406$) (Figure 7).

Figure 7. The UV-vis spectra ($\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$ ($\epsilon / \text{M}^{-1}\text{cm}^{-1}$)) of the representative verdazyl radical **4a**, together with a sketch of the model 6-oxo-verdazyl **B**, and plots of key molecular orbitals from **B** against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH_2Cl_2)). Contours plotted at $\pm 0.002\text{ (e/bohr}^3)^{1/2}$.

The frontier α - and β -spin orbitals of the extended model verdazyl 1,5-bis(phenylethynyl)-3-phenyl-6-oxoverdazyl (**C**) are topologically similar to those of **B** but contain appreciable contributions from the pendant phenylethynyl moieties (Figure 8). As a consequence, the ethynyl-functionalised compounds **8**, **9** and **10** are characterized by similar spectroscopic features as described for compounds **4a – c**, but shifted to lower energy due to the extended conjugation at the peripheral aryl rings (Figure 8, Figure S7), and accounting for the variation in colour of the compound in this series.

Figure 8. The UV-vis spectra ($\tilde{\nu}_{\text{max}} / \text{cm}^{-1}$ ($\epsilon / \text{M}^{-1}\text{cm}^{-1}$)) of the representative verdazyl radical **9**, together with a sketch of the model 'extended' 6-oxo-verdazyl **C**, and plots of key molecular orbitals against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH_2Cl_2)). Contours plotted at $\pm 0.002 \text{ (e/bohr}^3)^{1/2}$.

The TD-DFT calculations with model **C** (Figure 8, Table S4) assign the lowest energy absorption bands to the β -HOMO – β -LUMO transition ($\tilde{\nu} = 17104 \text{ cm}^{-1}$, $f = 0.2234$), likely overlapped with $[\beta\text{-HOMO-1}] - \beta\text{-LUMO}$ transition ($\tilde{\nu} = 18630 \text{ cm}^{-1}$, $f = 0.0464$) both of which offer charge transfer character from the tolane-like functionalities at rings X and Y to the heterocyclic core. At higher energies, the broad band centred near 25000 cm^{-1} likely arise from overlapping transitions which result in modest charge re-distribution from the verdazyl core to the peripheral tolane-like groups and the Z-aryl ring ($\alpha\text{-HOMO} - \alpha\text{-LUMO} / \beta\text{-[HOMO-2]} - \beta\text{-LUMO}$, $\tilde{\nu} = 22208 \text{ cm}^{-1}$, $f = 0.3422$; $\alpha\text{-HOMO} - \alpha\text{-LUMO} / \alpha\text{-HOMO} - \alpha\text{-[LUMO+2]}$, $\tilde{\nu} = 25911 \text{ cm}^{-1}$, $f = 0.4124$). The highest energy absorptions near $30,000 - 31,000 \text{ cm}^{-1}$ correspond to bands calculated to arise from mixed-orbital transitions in **C**, with overall $\pi\text{-}\pi^*$ character associated with the extended oligophenylene ethynylene fragments ($\tilde{\nu} = 31686 \text{ cm}^{-1}$, $f = 1.0785$).

EPR Spectra and Simulations.

The solution EPR spectra of all six examples of the radicals **4a – c**, **8**, **9** and **10** in dichloromethane at room temperature are shown in Figure 9 and exhibit a line-shape consistent with that previously described for 6-oxo-verdazyl derivatives.^{10, 53} The hyperfine structure can be rationalized in terms of the unpaired electron spin coupling to two sets of equivalent $I = 1$ nuclei i.e. two sets of equivalent nitrogen (^{14}N) atoms, consistent with the composition of the $\alpha\text{-HOMO}$ and $\beta\text{-LUMO}$ of the models **B** (Figure 7) and **C** (Figure 8) and spin density distribution (Figure S8).^{54, 55} For these compounds a 25-line pattern is predicted (Figure 9), although in the experimental data line broadening reduces the number of observed peaks to 19. All spectra are well-

modelled by the same or very similar parameters across all six radicals (Figure 9, Table 2). In each case, hyperfine couplings from the aromatic protons of the 6-oxo-verdazyl substituents all fall within the linewidth of the spectrum i.e. <6 MHz, as seen in earlier studies.¹⁰ Clearly the substituents introduced to the *para*-positions of the phenyl rings at the 1- and 5-positions of the 6-oxo-verdazyl cores in **4a – c** and **8**, **9** and **10** have little influence on the core spin density distribution.

Figure 9. Room-temperature solution cw-EPR spectra of the set of oxoverdazyl complexes.

Top: deconvolution of the hyperfine coupling pattern within the oxoverdazyl system. Bottom: experimental data (black trace) and spin Hamiltonian simulations (red dotted trace). Spectra were recorded at X-band microwave frequency (~ 9.4 GHz) with a field modulation amplitude of 0.5 G and a power of 0.47 mW. Samples were prepared in 100 μ M concentrations in dichloromethane (CH_2Cl_2) and degassed by sparging with Argon.

Table 2. Fitting parameters for simulations of cw-EPR spectra of the 6-oxo-verdazyl complexes **4c**, **8**, **9** and **10** shown in Figure 11.^a

Complex	g-value	Linewidth /mT	Hyperfine couplings /MHz	
			$a(\text{N}_{2,3})^b$	$a(\text{N}_{1,4})^b$
4a	2.0038	0.25	18.1	12.4
4b	2.0039	0.14	18.0	12.5
4c	2.0044	0.14	18.1	12.4
8	2.0041	0.15	18.0	12.0
9	2.0041	0.15	17.9	12.3
10	2.0043	0.15	18.0	12.5

^a Spectral features were modelled using the EasySpin package *garlic*.⁵⁶

^b Atom labels from Scheme 3.

Electrochemical and spectroelectrochemical studies

The verdazyl radicals **4a – c**, **8**, **9** and **10** are susceptible to both 1-electron oxidation and 1-electron reduction within a convenient electrochemical window, both processes being readily observed by cyclic and square-wave voltammetry at a platinum disc working electrode (Table 3, Figure S9, Figure S10). Whilst the oxidation of amine-functionalised **10** proved irreversible, the other verdazyls **4a – c**, **8** and **9** gave reversible oxidation processes together with a (quasi)reversible reduction in all cases.

Table 3. Summary of electrochemical data for compounds **4a – c** and **8 – 10**.^a

Compound	$E_{1/2}^{(\text{red})}$	$E_{1/2}^{(\text{ox})}$	$E_{1/2}^{(\text{ox})} - E_{1/2}^{(\text{red})}$
4a	−1.11	+0.41	1.52
4b	−1.03	+0.39	1.42
4c	−0.93	+0.53	1.46
8	−0.92	+0.49	1.41
9	−0.94	+0.49	1.43
10	−0.94	$E_p + 0.42^b$	

^a potentials referenced against an internal ferrocene / ferrocenium couple ($E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.00 \text{ V}$).

^b $E_{1/2}^{(\text{O})}$ of compound **10** obtained from square wave voltammetry is +0.38 V.

The UV-vis-NIR spectra of the redox products $[4a]^+$ and $[4a]^-$ collected by spectroelectrochemical methods provide a basis from which to further explore the redox products of 6-oxo-verdazyl compounds (Figure 10, Figure 11, Table S5). The spectral profiles of the redox generated products $[4b]^{+/-}$ (Figure S11) and $[4c]^{+/-}$ (Figure S12) are similar to those described for $[4a]^{+/-}$, clearly indicating the similar electronic characteristics of these species.

The prominent electronic absorption features in the electrochemically generated closed-shell cation $[4a]^+$ (Figure 10) are well modelled by TD-DFT calculations with $[B]^+$ (Table S3), and comparison of the frontier orbitals of the computational verdazyl model compounds **B** (Figure 7) and $[B]^+$ (Figure 10) indicates that the oxidation chemistry may be described in terms of depopulation of the α -HOMO of the 6-oxo-verdazyl precursor. The lowest energy feature in the spectroelectrochemically generated spectrum of $[4a]^+$ near 15800 cm^{-1} can be assigned to the HOMO – LUMO transition ($\tilde{\nu} = 14259\text{ cm}^{-1}$, $f = 0.1036$) which involves significant transfer of charge from the phenyl ring Z to the verdazyl core (Figure 10). The broad feature centred near $21,000\text{ cm}^{-1}$ can be attributed to a set of three excitations of mixed orbital origin, but which collectively had charge transfer character from the X and Y rings to the verdazyl core ($\tilde{\nu} = 19004\text{ cm}^{-1}$, $f = 0.3711$; $\tilde{\nu} = 19580\text{ cm}^{-1}$, $f = 0.0325$; $\tilde{\nu} = 22850\text{ cm}^{-1}$, $f = 0.1002$). The high-energy band above $35,000\text{ cm}^{-1}$ can be assigned to the HOMO – [LUMO+1] transition ($\tilde{\nu} = 33665\text{ cm}^{-1}$, $f = 0.5114$), which has π - π^* character, with a degree of charge transfer from the Z aryl group to the carbonyl moiety.

Figure 10. The spectroelectrochemically generated spectra of $[4a]^+$ together with a sketch of the model 6-oxo-verdazyl cation $[B]^+$, and plots of key molecular orbitals from $[B]^+$ against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH₂Cl₂)). Contours plotted at ± 0.002 (e/bohr³)^{1/2}.

The electronic structure of the model anion $[B]^-$ is appropriately described in terms of population of the β -LUMO of **B** (Figure 11). The experimental spectrum of the closed anion $[4a]^-$ is characterised by a weak low energy band envelope (Figure 11), which can be assigned by TD-DFT calculations carried out on $[B]^-$ (Table S3) as the HOMO – LUMO transition ($\tilde{\nu} = 19428$ cm^{-1} , $f = 0.0131$) and results in charge transfer from the verdazyl core and the X and Y rings to the Z aryl group. Based on the model TD-DFT results from $[B]^-$, the structured visible absorption envelope observed in the spectroelectrochemical experiment between ca. 25,000 – 30,000 cm^{-1} is attributed to a series of moderately intense transitions arising from the HOMO to [LUMO+1] ($\tilde{\nu} =$

22644 cm^{-1} , $f = 0.4037$) and the similarly comprised [LUMO+5] ($\tilde{\nu} = 29048 \text{ cm}^{-1}$, $f = 0.0715$), admixed with the HOMO – [LUMO+2] transition ($\tilde{\nu} = 24896 \text{ cm}^{-1}$, $f = 0.0794$). Collectively these processes result in charge transfer from the verdazyl core to the peripheral aryl groups X, Y and Z. The [HOMO-1] – LUMO transition ($\tilde{\nu} = 36685 \text{ cm}^{-1}$, $f = 0.2834$), with verdazyl π to Z aryl-group π^* character, accounts for the highest energy transition resolved in the spectroelectrochemical study of $[4a]^-$.

Figure 11. The spectroelectrochemically generated spectra of $[4a]^-$ together with a sketch of the model 6-oxo-verdazyl anion $[B]^-$, and plots of key molecular orbitals from $[B]^-$ against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH_2Cl_2)). Contours plotted at $\pm 0.002 \text{ (e/bohr}^3)^{1/2}$.

The chemical irreversibility of the oxidation of **10** prevented exploration of $[\mathbf{10}]^+$ within the spectroelectrochemical cell. In addition, attempts to use spectroelectrochemical methods to study the redox products derived from **8** were complicated by the low solubility of the redox products, which precipitated in the cell. However, compound **9** proved well-suited to spectroelectrochemical studies of both the one-electron oxidation and reduction products. The available spectroelectrochemical data (Figure 12, Figure 13) can be related to the results from TD-DFT calculations with the model compounds $[\mathbf{C}]^{+/-}$ (Figure 12, Figure 13, Table S4) and used to explore the effects of the extended conjugation at the 1- and 5-positions on the redox properties of the 6-oxo-verdazyl core.

On the basis of the TD-DFT calculations performed with $[\mathbf{C}]^+$, the lowest energy absorption bands in $[\mathbf{9}]^+$ are attributed to charge transfer-like transitions from the phenylene-ethynylene pendant groups to the verdazyl core (HOMO – LUMO, $\tilde{\nu} = 10368 \text{ cm}^{-1}$, $f = 1.1694$; [HOMO-1] – LUMO, $\tilde{\nu} = 13333 \text{ cm}^{-1}$, $f = 0.2112$), whilst the prominent feature at *ca.* $30,000 \text{ cm}^{-1}$ can be assigned to a series of over-lapping transitions with predominant charge transfer from the phenylene ethynylene groups to the Z group ([HOMO-1] – [LUMO+1], $\tilde{\nu} = 29186 \text{ cm}^{-1}$, $f = 0.3221$; HOMO – [LUMO+2], $\tilde{\nu} = 30346 \text{ cm}^{-1}$, $f = 0.3805$) and the verdazyl core ([HOMO-13] – LUMO, $\tilde{\nu} = 29531 \text{ cm}^{-1}$, $f = 0.2022$) (Figure 12).

Figure 12. The spectroelectrochemically generated spectra of $[9]^+$ together with a sketch of the model ‘extended’ 6-oxo-verdazyl cation $[C]^+$, and plots of key molecular orbitals from $[C]^+$ against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH₂Cl₂)). Contours plotted at ± 0.002 (e/bohr³)^{1/2}.

For the anions $[9]^-$ and $[10]^-$ there is little change in the overall appearance of the spectra relative to the neutral radical precursors, although the progress of the electrolysis of **9** and **10** to the monoanions is clearly evinced by the development of an isosbestic point in the spectroelectrochemical plots (Figure 13, Figure S13). TD-DFT calculations of the model anion $[C]^-$ (Figure 13) assign the experimentally observed features near 16,700 cm⁻¹ to the HOMO – LUMO transition ($\tilde{\nu} = 16018$ cm⁻¹, $f = 0.9501$) which has appreciable charge transfer character from the verdazyl core to the peripheral X and Y pendants. The features near 25,000 cm⁻¹ can likely be assigned to the overlapping HOMO – [LUMO+1] ($\tilde{\nu} = 19420$ cm⁻¹, $f = 0.1739$) and HOMO – [LUMO+2], ($\tilde{\nu} = 20725$ cm⁻¹, $f = 0.1362$) transitions which together have charge-transfer character from the core to the peripheral aryl rings X, Y and Z. The most

intense features above 30,000 cm^{-1} are attributed to the [HOMO-2] – LUMO, ($\tilde{\nu} = 30534 \text{ cm}^{-1}$, $f = 1.5889$) with π - π^* character along the tolan-like X and Y motifs.

Figure 13. The spectroelectrochemically generated spectra of [9]⁻ together with a sketch of the model 'extended' 6-oxo-verdazyl anion [C]⁻, and plots of key molecular orbitals from [C]⁻ against a schematic energy level diagram (B3LYP / 6-31G*(df,p)/COSMO(CH₂Cl₂)). Contours plotted at $\pm 0.002 \text{ (e/bohr}^3)^{1/2}$.

For each system examined here it is clear that the heterocyclic core plays a significant role in both supporting the unpaired electron and serving as the primary site for the redox reactions. However, the introduction of the phenyl-ethynyl fragments to the phenylene X and Y rings at the 1- and 5-positions of the 6-oxo-verdazyl core results in an additional contribution from the extended π -conjugation system to the frontier orbitals of the model compounds [C]^{+0/-}, and a degree of fine-tuning of the optical properties of the experimental systems **8** – **10**. The introduction of substituents at the 1-

and 5-positions of the verdazyl core can therefore be identified as a route to optimising the materials properties of these remarkably stable, readily prepared radicals.

The orbital topologies of the model systems $[\mathbf{B}]^{+/0/-}$ and $[\mathbf{C}]^{+/0/-}$ also deserve comment in the wider context of the use of such compounds as components within molecular electronic junctions.^{57, 58} The structure of the HOMO and LUMO is known to influence molecular conductance, and recently highlighted orbital product rules serve as tools for discovery of quantum interference phenomena.⁵⁹⁻⁶¹ In brief, the rules provide a qualitative indication for the presence (or absence) of destructive quantum interference (DQI) features in the transmission function, $T(E)$, from the relative phases of the HOMO and LUMO at the site of contact to the electrodes. If the phase of the amplitudes of the HOMO (LUMO) at the electrode contacts have the same sign, the orbital product $a_H \cdot a_L$ is positive, the HOMO and LUMO will interfere destructively and a DQI feature is likely to be found in $T(E)$. However, if the phase of the amplitudes are different, the orbital product $a_H \cdot a_L$ is negative, and constructive quantum interference (CQI) phenomena are likely. An inspection of the frontier molecular and spin orbitals of $[\mathbf{B}]^{+/0/-}$ and $[\mathbf{C}]^{+/0/-}$ indicates that, in principle, each system should display CQI, despite the *meta*-like position of the anchor groups at the 6-membered verdazyl core (Figure 14). Such observations motivate future efforts to explore the electrical properties of verdazyl-based molecular junctions.

	β -HOMO	β -LUMO	$a_H \cdot a_L$
B	$a_H = +$	$a_L = -$	$-$ CQI
C	$a_H = +$	$a_L = -$	$-$ CQI
	HOMO	LUMO	$a_H \cdot a_L$
[B]⁺	$a_H = +$	$a_L = -$	$-$ CQI
[B]⁻	$a_H = -$	$a_L = +$	$-$ CQI
[C]⁺	$a_H = +$	$a_L = -$	$-$ CQI
[C]⁻	$a_H = -$	$a_L = +$	$-$ CQI

Figure 14. Plots of the (β -)HOMOs and (β -)LUMOs of molecules $[B]^{-/0/+}$ and $[C]^{-/0/+}$

and indicative outcomes of the predictions for CQI from the orbital product rule.^{59,60} By way of example, the β -HOMO of **B** has the same phase at the *para*-positions of the X and Y rings (each arbitrarily designated as +) and is assigned a positive orbital product, $a_H = +$. These positions are out of phase in the β -LUMO (and distinguished by arbitrary + and – values in the plots above), and the orbital product is assigned a negative value, $a_L = -$. The product of $a_H \cdot a_L$ is negative, and hence **B** is predicted to exhibit CQI.

Conclusion

A series of 6-oxo-verdazyl radicals, including an example bearing surface contacting thiomethyl groups at the 1- and 5-positions (**4b**), have been readily prepared using conventional synthetic strategies. The 1,5-di(4-iodophenyl)-3-phenyl-6-oxo-verdazyl radical (**4c**) serves as an entry point to a further series of ethynyl substituted 6-oxo-verdazyl radicals through Sonogashira cross-coupling reactions with terminal alkynes. The introduction of the extended π -systems at the 1,5-positions results in further delocalisation of the frontier molecular (spin) orbitals, which is evinced in the optical spectra of these derivatives. The radicals undergo both one-electron reduction and oxidation with spectroelectrochemical studies together with TD-DFT calculations on model systems consistent with the redox events arising from population of the β -LUMO and depopulation of the α -HOMO.

Experimental

General information

All reactions were carried out under nitrogen using standard Schlenk procedures, but no special methods were used during work up. Toluene was dried on an InertTM solvent

purification system, diisopropylamine was dried and distilled from KOH. Other reaction solvents were used as received, and all solvents were degassed by sparging with nitrogen before use. The compounds 4-iodophenylhydrazine,⁶² 4-ethynylaniline,⁶³ (4-ethynylphenyl)(methyl)sulfane,⁶⁴ and 5-ethynyl-3,3-dimethyl-2,3-dihydrobenzo[*b*]thiophene⁶⁵ were prepared according to the literature procedures. Other reagents were purchased and used as received.

NMR data were collected on 400 MHz Varian, 500 MHz Bruker and 600 MHz Bruker machines. ¹H and ¹³C{¹H} NMR spectra were referenced to deuterio or residual protio solvent signals (CDCl₃: δ 7.26 ppm, δ 77.16 ppm; (CD₃)₂SO: δ 2.50 ppm, δ 39.52 ppm; CD₂Cl₂: δ 5.32 ppm, δ 53.84 ppm). IR spectra were recorded on a Cary 630 FTIR Spectrometer in the ATR mode. Mass spectra were collected on a Waters Liquid Chromatograph Premier Mass Spectrometer in positive ion electrospray ionisation (ESI+) or Atmospheric-Pressure Chemical Ionisation mode (APCI+) mode. NMR and mass spectra for each compound are given in the ESI (Figures S14-S37). Static UV-vis-NIR spectra of the compounds in CH₂Cl₂ solutions were recorded in a quartz cell of pathlength 1 cm using a Cary 5000 UV-vis-NIR spectrometer. Cyclic voltammetry was conducted in a standard three-electrode cell, with Pt disc working electrode, Pt wire counter and Pt wire pseudo-reference electrodes, from solutions in 0.1 M NBu₄PF₆ / CH₂Cl₂, with data collected from an EmStat3+ potentiostat. The ferrocene/ferrocenium ($E_{1/2}$ = 0 V) and decamethyl ferrocene/ decamethyl ferrocenium couples ($E_{1/2}$ = -0.55 V versus ferrocene / ferrocenium)⁶⁶ were used as internal references for potential measurements. Spectroelectrochemical studies were conducted in a transmission cell of Hartl design fitted with CaF₂ windows,⁶⁷ and controlled by the

EmStat3+ from solutions of the analyte (ca. 1 mM) in 0.1 M NBu₄PF₆ / CH₂Cl₂. Data were recorded on Cary 5000 UV-vis-NIR and Cary 660 FTIR/NIR spectrometers.

Crystallography. Data were collected with a Rigaku-Oxford Gemini, Xcalibur diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) for compound **4c** and a Rigaku-Oxford Diffraction XtaLAB Synergy-S diffractometer using a micro-focus sealed Cu K α radiation (λ = 1.54184 Å) X-ray source for compounds **2a**, **3a-c**, **4a** and **4b**. All data were reduced using the CrysAlis Pro software.⁶⁸ The molecular structures were solved by intrinsic phasing using SHELXT⁶⁹ within Olex2⁷⁰ (**2a**, **3a-c**, **4a**, **4b**) or by direct methods using the SHELXS⁷¹ program implemented within WinGX⁷² (**4c**). Structures were refined by full-matrix least-squares procedures on F^2 using Crystals⁷³ (**3c**), or SHELXL⁷⁴ (**2a**, **3a-c**, **4a**, **4b**). All non-hydrogen atoms were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions. Graphics of the molecular structures have been created by using Diamond.⁷⁵ Compound **3c** and **4c** were refined as 3- and 2-component twins, respectively. The three twin laws for **3c** were found using the program ROTAX⁷⁶ within Crystals. The crystal of **4c** showed two domains and was thus integrated as a twin and merged into a hklf5 file with a scale factor of 0.704:0.296. Further crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data with CCDC numbers 2109616 - 2109622 can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk).

Computational details. Calculations were performed using the Gaussian09 software package,⁷⁷ and visualised with GaussView05⁷⁸ and further analysed with the GaussSum3.0 package.⁷⁹ The geometries of the compounds were optimized at the density functional theory (DFT) level with the B3LYP functional,^{80, 81} and 6-31G*(df,p) basis set,^{82, 83} and COSMO(CH₂Cl₂) solvent model.⁸⁴

EPR Measurements. Spectra of 6-oxo-verdazyl compounds were recorded from 100 μ M solutions in CH₂Cl₂, degassed by sparging with Argon gas for 15 minutes prior to measurement. Samples were measured in Q-band capillaries (0.3 mm ID), placed inside an X-band quartz tube to minimize microwave dampening by CH₂Cl₂. Continuous Wave (cw-EPR) measurements were performed at room temperature on a Bruker E500 spectrometer equipped with an ER4122 SHQ resonator. Spectra were recorded with a field modulation amplitude of 0.5 G and a power of 0.47 mW.

Spectra were simulated using the EasySpin package in MATLAB using the isotropic and fast-motion cw-EPR program *garlic*.⁵⁶ Simulations were optimized using a Nelder-Mead minimization algorithm. A Voigtian linewidth (Gaussian + Lorentzian) was used.

[4-Methylphenyl]hydrazine:⁸⁵ A Schlenk flask was charged with 4-methylaniline (4.01 g, 37.3 mmol) in 32% (w) HCl (60 mL). The slurry was heated to 120 °C until a turbid solution was formed. The solution was cooled to −5 °C and a solution of NaNO₂ (3.09 g, 44.8 mmol) in H₂O (28 mL) was added dropwise while maintaining the temperature at −5 °C. The mixture was stirred at this temperature for 2 hours before

being added via canula to a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (25.3 g, 119 mmol) in 32% HCl (12 mL) at $-20\text{ }^\circ\text{C}$. After stirring at $-20\text{ }^\circ\text{C}$ for 30 minutes the reaction mixture was allowed to warm to $-5\text{ }^\circ\text{C}$ and stirred for another 30 minutes. The precipitate formed was collected by filtration, which was then suspended in 1M $\text{NaOH}_{(\text{aq})}$ solution to liberate the desired hydrazine. The suspension was extracted using diethyl ether (2 x 100 ml) and the combined organic extracts were washed with brine and water, dried under MgSO_4 and the volatiles removed under reduced pressure to afford the desired compound as a yellow-coloured, hygroscopic solid (2.5 g, 54%). The precipitate formed a dark viscous liquid upon standing in air and the NMR indicated signs of decomposition. The solid product obtained was therefore used immediately without further purification. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.95 (d, $J = 8.5\text{ Hz}$, 2H), 6.74 (d, $J = 8.5\text{ Hz}$, 2H), 2.28 (s, 3H, CH_3).

1-Benzylidene-2-(4-methylphenyl)hydrazine (1a):⁸⁶ A solution of [4-methylphenyl]hydrazine (0.50 g, 4.1 mmol) and benzaldehyde (0.54 mL, 5.3 mmol) in ethanol (40 mL) was treated with a catalytic amount of formic acid before the solution was heated at reflux overnight. After this time, the solvent was removed under reduced pressure, the residue was washed with hexanes and dried under vacuum to give **1a** as pale white solid (0.39 g, 45%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.65 (d, $J = 7.6\text{ Hz}$, 3H), 7.37 (t, $J = 7.5\text{ Hz}$, 2H), 7.29 (t, $J = 7.3\text{ Hz}$, 1H), 7.09 (d, $J = 8.2\text{ Hz}$, 2H), 7.03 (d, $J = 8.2\text{ Hz}$, 2H), 2.30 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3): δ 142.6, 136.9,

135.6, 129.9, 129.5, 128.7, 128.4, 126.2, 113.05, 20.7. **ESI(+)-MS:** m/z 211.1231 [(M+H)⁺ calculated 211.1235].

2-Benzylidene-1-(4-methylphenyl)hydrazine-1-carbonyl chloride (2a): To a solution of triphosgene (0.14 g, 0.31 mmol) in dry toluene (15 mL) at 0 °C, a solution of **1a** (0.20 g, 0.95 mmol) in ethyl acetate (15 mL) and pyridine (84 μ L, 1.0 mmol) was added dropwise. Following the addition, mixture was heated at 60°C for 45 minutes. After allowing to cool to room temperature, the mixture was filtered over a pad of Celite, and solvents were removed under reduced pressure. The residue was washed with hexanes before being extracted into diethyl ether. Slow removal of diethyl ether from the extract gave **2a** as white crystals suitable for X-ray diffraction studies (0.19 g, 73%). **¹H NMR** (500 MHz, CDCl₃): δ 7.65 (dd, J = 7.5, 2.0 Hz, 2H), 7.39 (dd, J = 4.4, 3.6 Hz, 5H), 7.37 (s, 1H, CH), 7.15 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H, CH₃). **¹³C{¹H} NMR** (500 MHz, CDCl₃): δ 145.6, 140.7, 131.3, 130.8, 128.9, 128.7, 128.0, 21.5. **IR** (solid, ATR): ν (C=O) 1730(s) cm⁻¹. **ESI(+)-MS:** m/z 273.0794 [(M+H)⁺ calculated 273.0795].

2,4-Bis(4-methylphenyl)-6-phenyl-1,2,4,5-tetrazinan-3-one (3a): To a saturated solution of [4-methylphenyl]hydrazine (0.13 g, 1.1 mmol) in ethanol (20 mL), **2a** (0.15 g, 0.55 mmol) was added in portions resulting in the immediate formation of a precipitate. After stirring the mixture overnight, the precipitate was collected by filtration, washed with diethyl ether and dried under reduced pressure to obtain **3a** as a white flaky solid (0.07 g, yield 36%). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a CD₂Cl₂ solution. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.57 (dd, J = 7.3, 1.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 4H), 7.41 – 7.36 (m, 3H), 7.16 (d, J = 8.2 Hz, 4H), 5.46 (t, J = 10.2 Hz, 1H), 4.81 (d, J = 10.2 Hz, 2H), 2.34 (s, 6H, CH₃). ¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 156.1, 140.3, 136.5, 134.7, 129.3, 129.2, 129.1, 126.9, 122.6, 73.1, 21.0. IR (solid, ATR): ν (NH) 3226(s); ν (C=O) 1620(s) cm⁻¹. ESI(+)-MS: m/z 359.1872 [(M+H)⁺ calculated 359.1872].

1,5-Di(4-methylphenyl)-3-phenyl-6-oxo-verdazyl radical (4a): To a solution of **3a** (0.05 g, 0.14 mmol) in dichloromethane (15 mL) and methanol (5 mL), sodium metaperiodate (0.30 g, 1.4 mmol) was added. The solution was heated at 50°C overnight, after which time the solution had become a dark pink colour, and TLC

analysis indicated the complete consumption of starting material. The solution was cooled, filtered and the filtrate evaporated to dryness. The residue was purified by preparative thin layer chromatography eluting with dichloromethane and hexane (2:1). The prominent purple band was collected to give **4a** as a dark pink solid (0.03 g, 65%) and recrystallised by slow evaporation of toluene to afford crystals suitable for X-ray diffraction. **IR** (solid, ATR): $\nu(\text{C}=\text{O})$ 1702(s) cm^{-1} . **ESI(+)-MS**: m/z 356.1637 $[(\text{M}+\text{H})^+ \text{ calculated } 356.1637]$. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_4\text{O}^+$: C, 74.35; H, 5.39; N, 15.76. Found: C, 74.40; H, 5.33; N, 15.89.

[4-(Thiomethyl)phenyl]hydrazine.⁸⁷ A Schlenk flask was charged with 4-(thiomethyl)aniline (2.0 mL, 16 mmol) in 32% HCl (32 mL). The slurry was heated to 120 °C until a violet solution was formed. The solution was cooled to -5 °C and a solution of NaNO_2 (1.22 g, 17.7 mmol) in H_2O (14 mL) was added dropwise maintaining the temperature at -5 °C. The mixture was stirred for 2 hours and transferred through canula to a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (10.9 g, 48.3 mmol) in 32% HCl (12 mL) at -20 °C resulting in the formation of a copious white precipitate. After stirring at -20 °C for 30 minutes, the solution was warmed to -5 °C and stirred further for another 30 minutes. The precipitate was collected by filtration and the hydrazine hydrochloride was neutralised by suspension in a 1 M $\text{NaOH}_{(\text{aq})}$ solution. The resulting suspension of the hydrazine was extracted using diethyl ether (2 x 100 ml) and the combined organic extracts were washed with brine, dried under MgSO_4 and the solvents removed under reduced pressure to obtain the desired product as a yellow hygroscopic solid (1.6 g, 63%). The product obtained was used without further

purification. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.17 (d, $J = 8.7$ Hz, 2H), 6.70 (d, $J = 8.7$ Hz, 2H), 5.07 (s, br, 1H, NH), 3.50 (s, br, 2H, NH_2), 2.35 (s, 3H, CH_3).

1-Benzylidene-2-(4-[Thiomethyl]phenyl)hydrazine (1b): A Schlenk flask was charged with a solution of [4-(thiomethyl)phenyl]hydrazine (0.60 g, 3.9 mmol) and benzaldehyde (0.52 mL, 5.1 mmol) in ethanol (50 mL). The mixture was heated at reflux for 2 hours. After this, the solution was cooled to room temperature and the volatiles were removed under reduced pressure. The obtained residue was washed with hexanes and vacuum dried to afford **1b** as light brown solid (0.71 g, 75%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.70 (s, 1H, CH), 7.66 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.27 (dd, $J = 6.7, 1.9$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 2.46 (s, 3H, CH_3). **ESI-MS(+):** m/z 243.0956 [$(\text{M}+\text{H})^+$ calculated 243.0956].

2-Benzylidene-1-[4-(Thiomethyl)phenyl]hydrazine-1-carbonyl chloride (2b): To a solution of triphosgene (0.31 g, 1.0 mmol) in dry toluene (30 mL) maintained at 0°C was added a solution of **1b** (0.50 g, 2.1 mmol) in ethyl acetate (30 mL) and pyridine

(183 μ L, 2.30 mmol) dropwise. The mixture was then heated at 60°C for 45 minutes. After allowing the solution to cool to room temperature, the mixture was filtered over a Celite plug and the solvents were removed under reduced pressure. The residue was washed with hexanes and then extracted using diethyl ether. Removal of ether yielded **2b** as a white powder (0.57 g, 91%). **¹H NMR** (500 MHz, CDCl₃): δ 7.52 (d, J = 7.7 Hz, 6H), 7.26 (dd, J = 9.2, 7.4 Hz, 6H), 7.13 (s, 1H, CH), 7.04 (d, J = 8.4 Hz, 2H), 2.42 (s, 3H, CH₃). **¹³C{¹H} NMR** (600 MHz, CDCl₃): δ 145.6, 142.2, 133.4, 132.6, 129.3, 128.9, 128.0, 127.6, 15.4. **IR** (solid, ATR): ν (C=O) 1728(s) cm⁻¹. **ESI-MS(+)**: m/z 305.0515 [(M+H)⁺ calculated 305.0515].

2,4-Bis[4-(Thiomethyl)phenyl]-6-phenyl-1,2,4,5-tetrazinan-3-one (3b): To a saturated solution of [4-(Thiomethyl)phenyl]hydrazine (0.45 g, 2.9 mmol) in ethanol (35 mL), **2b** (0.45 g, 1.5 mmol) was added in portions. After stirring the solution overnight, the resulting precipitate was collected by filtration solids, washed with diethyl ether and dried under vacuum to obtain **3b** as a white flaky solid (0.39 g, yield 62%). Crystals suitable for X-ray diffraction were obtained from slow evaporation of a CDCl₃ solution. **¹H NMR** (600 MHz, (CD₃)₂SO): δ 7.54 (d, J = 8.8 Hz, 4H), 7.52 (d, J = 7.2 Hz, 2H), 7.34 (dt, J = 13.8, 7.0 Hz, 3H), 7.24 (d, J = 8.9 Hz, 4H), 6.38 (d, J = 9.0 Hz, 2H, NH), 5.37 (t, J = 8.9 Hz, 1H), 2.46 (s, 6H, CH₃). **¹³C{¹H} NMR** (600 MHz, (CD₃)₂SO): δ 156.3, 140.3, 137.5, 132.1, 128.3, 128.2, 127.0, 126.4, 122.0, 72.5, 15.6.

IR (solid, ATR): $\nu(\text{NH})$ 3246(s); $\nu(\text{C=O})$ 1628(s) cm^{-1} . **ESI-MS(+)**: m/z 423.1313 [(M+H)⁺ calculated 423.1313].

1,5-Di(4-thiomethyl-phenyl)-3-phenyl-6-oxo-verdazyl radical (4b): To a solution of **3b** (0.05 g, 0.12 mmol) in dichloromethane (15 mL) and methanol (5 mL) was added sodium metaperiodate (0.25 g, 1.2 mmol). The solution was heated at 50°C for 3 hours during which the colour changed to deep violet. The solution was allowed to cool to room temperature and filtered. The filtrate was evaporated to dryness and the residue was purified by preparative thin layer chromatography. Prior to purification, the plates were neutralised with 1% Triethylamine and hexane mixture to avoid tailing of the compound and the prominent violet band was eluted with dichloromethane and hexane (2:1). The desired product was obtained as a deep violet crystalline solid (0.03 g, 65%), which was recrystallised by slow evaporation of a toluene solution. **IR** (solid, ATR): $\nu(\text{C=O})$ 1697(s) cm^{-1} . **ESI-MS(+)**: m/z 420.1082 [(M+H)⁺ calculated 420.1078]. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_4\text{OS}_2$: C, 62.98; H, 4.56; N, 13.35. Found: C, 62.61; H, 4.58; N, 13.37.

[4-Iodophenyl]hydrazine:⁶² To a suspension of 4-iodoaniline (3.00 g, 13.6 mmol) in 20% HCl (16 mL) maintained at 0°C, an ice cold solution of NaNO_2 (0.98 g, 14 mmol)

in water (65 mL) was added dropwise. The solution was stirred at 0°C for 1 hour before being added to a solution of SnCl₂·2H₂O (8.01 g, 35.5 mmol) in 32% HCl (11 mL) at 0°C. After the addition, a copious white precipitate was formed and the stirring was continued for another 30 minutes at room temperature. The precipitate was then collected through filtration and the solids suspended in a 1M NaOH_(aq) solution to liberate the hydrazine. The solids were collected by filtration, and the solid mass extracted CH₂Cl₂ (2 x 100 mL). The combined organic extract was dried over MgSO₄, filtered and the solvents were evaporated under reduced pressure to obtain [4-iodophenyl]hydrazine (2.3 g, 72%) as a yellow solid. The product obtained was used without further purification. ¹H NMR (600 MHz, CDCl₃): δ 7.49 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.19 (bs, 1H, NH), 3.55 (s, 2H, NH₂).

1-Benzylidene-2-(4-iodophenyl)hydrazine (1c):⁸⁸ A solution of [4-iodophenyl]hydrazine (2.34 g, 10.0 mmol) and benzaldehyde (1.32 mL, 13.0 mmol) in ethanol (50 mL) was heated to reflux overnight. After cooling to room temperature, ethanol was removed under reduced pressure. The obtained residue was washed with hexane and dried to obtain **1c** as a light brown solid (2.5 g, 76%). ¹H NMR (CDCl₃): δ 7.683 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.60 (s, br, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H).

2-Benzylidene-1-(4-iodophenyl)hydrazine-1-carbonyl chloride (2c): To a solution of triphosgene (0.58 g, 1.9 mmol) in dry toluene (20 mL) at 0°C, a solution of **1c** (1.14 g, 3.50 mmol) in ethyl acetate (20 mL) and pyridine (310 μ L, 3.85 mmol) was added dropwise. After addition, the mixture was heated at 60°C for 45 minutes. After cooling to room temperature, the mixture was filtered over a pad of Celite and the solvents were removed by rotatory evaporation. The obtained residue was washed with hexanes and then extracted into diethyl ether. Removing the ether from the extract left **2c** as white powder (1.3 g, 94%). $^1\text{H NMR}$ (CDCl_3): δ 7.93 (d, J = 8.6 Hz, 2H), 7.66 (dd, J = 7.9, 1.6 Hz, 2H), 7.40 (m, 4H), 7.02 (d, J = 8.5 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, CDCl_3): δ 146.4, 142.0, 136.0, 133.2, 131.1, 130.8, 129.0, 128.0, 96.4. IR (solid, ATR): $\nu(\text{C=O})$ 1719(s) cm^{-1} . APCI-MS(+): m/z 384.9606 [(M+H) $^+$ calculated 384.9605].

2,4-Bis(4-iodophenyl)-6-phenyl-1,2,4,5-tetrazinan-3-one (3c): To a saturated solution of [4-iodophenyl]hydrazine (0.94 g, 4.0 mmol) in ethanol (15 mL) **2c** (0.77 g, 2.0 mmol) was added in portions at room temperature. After stirring for overnight, the mixture was filtered by suction and the solid was washed with diethyl ether and

vacuum dried to get the desired product as a light brown solid (0.79 g, 67%). Slow evaporation of a CDCl_3 solution afforded crystals suitable for X-ray diffraction. ^1H NMR (CDCl_3): δ 7.66 (d, J = 9.0 Hz, 4H), 7.53 (d, J = 7.4, 1.6 Hz, 2H), 7.46 (d, J = 9.0 Hz, 4H), 7.40 (m, 3H), 5.49 (t, J = 10.0 Hz, 1H), 4.72 (d, J = 10.1 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, (CDCl_3): δ 156.2, 141.7, 137.6, 135.6, 129.4, 129.2, 126.5, 123.3, 88.4, 73.4. IR (solid, ATR): $\nu(\text{NH})$ 3244(s); $\nu(\text{C=O})$ 1625(s) cm^{-1} . APCI-MS(+): m/z 582.9492 $[(\text{M}+\text{H})^+]$ calculated 582.9492].

1,5-Di(4-iodophenyl)-3-phenyl-6-oxo-verdazyl radical (4c): To a solution of **3c** (0.50 g, 0.85 mmol) in dichloromethane (60 mL) and methanol (15 mL) was added sodium metaperiodate (1.8 g, 8.5 mmol) and the reaction mixture heated at 50°C . The solution became violet red immediately and was allowed to stir for 5 hours. After cooling down to room temperature, the solution was filtered and the filtrate was evaporated to dryness. The residue was purified by silica gel chromatography with dichloromethane and hexane (1:1) as eluent. The second and prominent band (violet red) was collected to yield **4c** as a violet red crystalline solid (0.36 g, 73%) and recrystallised by slow evaporation of a CH_2Cl_2 solution. IR (solid, ATR): $\nu(\text{C=O})$ 1688(s) cm^{-1} . APCI-MS(+): m/z 579.9259 $[(\text{M}+\text{H})^+]$ calculated 579.9257]. Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{I}_2\text{N}_4\text{O}^\bullet$: C, 41.48; H, 2.26; N, 9.67. Found: C, 41.70; H, 2.14; N, 9.62.

2,4-Bis(4-((4-(methylthio)phenyl)ethynyl)phenyl)-6-phenyl-1,2,4,5-tetrazinan-3-

one (5): A Schlenk flask was charged with diisopropylamine (100 mL) and (4-ethynylphenyl)(methyl)sulfane (0.430 g, 2.93 mmol) and degassed thoroughly. Then **3c** (0.64 g, 1.1 mmol), PdCl₂(PPh₃)₂ (15 mg, 0.02 mmol) and CuI (8.0 mg, 0.04 mmol) were added and the mixture was stirred overnight. The solvent was removed under reduced pressure and the residue was washed with a mixed solvent of hexane and diethyl ether (1/1), water and hexane. Eluting through silica gel column with dichloromethane yielded the product as a pale yellow solid (0.62 g, 91%). **¹H NMR** (600 MHz, (CD₃)₂SO): δ 7.69 (d, *J* = 8.7 Hz, 4H), 7.52 (d, *J* = 8.6 Hz, 6H), 7.47 (d, *J* = 8.3 Hz, 4H), 7.38-7.32 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 4H), 6.50 (d, *J* = 9.0 Hz, 2H), 5.43 (t, *J* = 8.9 Hz, 1H), 2.504 (s, 6H). **¹³C{¹H} NMR** (600 MHz, (CD₃)₂SO): δ 158.0, 142.7, 139.4, 137.9, 131.6, 131.3, 128.4, 128.263 126.1, 125.6, 120.0, 118.5, 116.4, 89.6, 88.5, 73.5, 14.2. **IR** (solid, ATR): ν(NH) 3227(br, m), 3206(w); ν(C≡C) 2113(br, w); ν(C=O) 1624(s) cm⁻¹. **ESI(+)-MS**: *m/z* 623.1939 [(M+H)⁺ 623.1939].

2,4-Bis(4-((3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl)ethynyl)phenyl)-6-phenyl-1,2,4,5-tetrazinan-3-one (6): To a Schlenk flask containing degassed diisopropylamine (12 mL) and tetrahydrofuran (8 mL), (4-ethynylphenyl)(methyl)sulfane (0.10 g, 0.54 mmol) was added. Then **3c** (0.14 g, 0.23 mmol), PdCl₂(PPh₃)₂ (8.0 mg, 0.02 mmol) and CuI (2.0 mg, 0.02 mmol) were added and the mixture was stirred at room temperature for 24 hours. The solvents were removed under reduced pressure and the crude product was purified by silica gel chromatography with dichloromethane and hexane (2:1) as eluent to yield **6** as a pale white solid (0.12 g, 74%). ¹H NMR (600 MHz, (CD₃)₂SO): δ 7.66 (d, *J* = 8.7 Hz, 4H), 7.52 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 4H), 7.40 (m, 3H), 7.28 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.20 (d, *J* = 1.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.40 (t, *J* = 10.1 Hz, 1H), 4.71 (d, *J* = 10.1 Hz, 2H), 3.20 (s, 4H), 1.39 (s, 12H). ¹³C{¹H} NMR (600 MHz, CDCl₃): δ 155.9, 148.4, 141.6, 141.5, 137.5, 135.7, 131.9, 130.9, 129.2, 129.0, 126.6, 125.9, 123.5, 122.4, 121.0, 119.3, 119.2, 89.7, 88.9, 73.2, 47.4, 27.5. IR (solid, ATR): ν(NH) 3240(br, w); ν(C≡C) 2112(br, w); ν(C=O) 1636(s) cm⁻¹. ESI-MS(+): *m/z* 703.2564 [(M+H)⁺ calculated 703.2565].

2,4-Bis(4-((4-aminophenyl)ethynyl)phenyl)-6-phenyl-1,2,4,5-tetrazinan-3-one (7):

To a degassed solution of diisopropylamine (15 mL) and tetrahydrofuran (5 mL), **3c** (0.30 g, 0.52 mmol), 4-ethynylaniline (0.13 g, 1.1 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (18 mg, 0.03 mmol) and CuI (5.0 mg, 0.03 mmol) were added and the mixture was stirred overnight at room temperature. After the complete consumption of **3c** (monitored by TLC), the volatiles were removed under reduced pressure and the crude product was purified by silica gel chromatography with dichloromethane and hexane (6:1) as eluent to yield **7** as a pale yellow solid (0.24 g, 84%). $^1\text{H NMR}$ (600 MHz $(\text{CD}_3)_2\text{SO}$): δ 7.64 (d, $J = 8.8$ Hz, 4H), 7.52 (d, $J = 6.9$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 4H), 7.38-7.32 (m, 3H), 7.19 (d, $J = 8.5$ Hz, 4H), 6.56 (d, $J = 8.5$ Hz, 4H), 6.47 (d, $J = 9.0$ Hz, 4H), 5.53 (bs, 4H), 5.42 (t, $J = 9.0$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$): δ 157.7, 149.3, 142.0, 137.9, 132.4, 130.8, 128.4, 128.2, 126.9, 120.2, 117.7, 113.7, 108.4, 90.4, 86.6, 73.3. IR (solid, ATR): $\nu(\text{NH})$ 3218(br, m); $\nu(\text{C}\equiv\text{C})$ 2112(br, w); $\nu(\text{C}=\text{O})$ 1618(s) cm^{-1} . ESI-MS(+): m/z 561.2407 $[(\text{M}+\text{H})^+ \text{calculated } 561.2403]$.

1,5-Bis(4-((4-(methylthio)phenyl)ethynyl)phenyl)-3-phenyl-6-oxo-verdazyl radical (8): To a degassed solution of diisopropylamine (15 mL) and tetrahydrofuran (5 mL), **4c** (0.09 g, 0.15 mmol), (4-ethynylphenyl)(methyl)sulfane (0.05 g, 0.36 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (5.0 mg, 0.01 mmol) and CuI (2.0 mg, 0.01 mmol) were added and the mixture was stirred overnight at room temperature. The solvents were removed under reduced pressure and the crude product was extracted with dichloromethane and water (1:1) dried under MgSO_4 to obtain a dark blue green precipitate. It was then washed with a mixed solvent of hexane and diethyl ether (1:1) to obtain **8** as a dark greenish blue solid (0.08 g, 84%).

The radical **8** could also be synthesized by heating **5** (0.02 g, 0.03 mmol) in dichloromethane (10 mL) and methanol (5 mL) in presence of NaIO_4 (0.07, 0.32 mmol) as the oxidant. After 5 hours, the solution was cooled, filtered and solvents were removed under reduced pressure to obtain a dark green solid, which was washed with diethylether and hexane to afford **8** as a dark greenish blue solid (6.0 mg, 30%). **IR** (solid, ATR): $\nu(\text{C}\equiv\text{C})$ 2113(br, w); $\nu(\text{C}=\text{O})$ 1694(s) cm^{-1} . **APCI-MS(+)**: m/z 620.1704 $[(\text{M}+\text{H})^+ \text{ calculated } 620.1705]$.

1,5-Bis(4-((3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl)ethynyl)phenyl)-3-

phenyl-6-oxo-verdazyl radical (9): To a Schlenk flask containing degassed diisopropylamine (15 mL) and tetrahydrofuran (5 mL), (4-ethynylphenyl)(methyl)sulfane (0.05 g, 0.28 mmol) was added. It was then followed by the addition of **4c** (0.07 g, 0.12 mmol), PdCl₂(PPh₃)₂ (4.0 mg, 0.01 mmol) and CuI (1.0 mg, 0.01 mmol). The mixture was stirred at room temperature for 24 hours. After which, the solvents were removed under reduced pressure and the crude product was purified by silica gel chromatography with dichloromethane and hexane (2:1) to yield **9** as a green crystalline solid (0.08 g, 93%).

This radical could also be synthesized the by oxidation of **6** (0.02 g, 0.03 mmol) using NaIO₄ (0.06, 0.28) as the oxidant by gently heating in dichloromethane (10 mL) and methanol (5 mL) for 5 hours. After cooling the reaction solution to room temperature, the solution was filtered and the filtrate was evaporated to dryness to give a dark green residue, which was purified by silica gel chromatography. Elution with dichloromethane and hexane (1:2) afforded **9** as a green crystalline solid (0.01 g, 45%).

IR (solid, ATR): $\nu(\text{C}\equiv\text{C})$ 2111(br, w); $\nu(\text{C}=\text{O})$ 1698(s) cm⁻¹. **APCI-MS(+)**: m/z 700.2330 [(M+H)⁺ calculated 700.2330]. Anal. Calcd for C₄₄H₃₅N₄OS₂[•]: C, 75.51; H, 5.04; N, 8.01. Found: C, 75.07; H, 4.95; N, 7.93.

1,5-Bis(4-((4-aminophenyl)ethynyl)phenyl)-3-phenyl-6-oxo-verdazyl radical (10):

A Schlenk flask was charged with diisopropylamine (15 mL) and tetrahydrofuran (5 mL), and degassed by sparging with N₂. To this solution, 4-ethylaniline (0.04 g, 0.36 mmol), **4c** (0.10 g, 0.17 mmol), PdCl₂(PPh₃)₂ (6.0 mg, 0.01 mmol) and CuI (2.0 mg, 0.01 mmol) were added and the mixture was stirred for 24 hours at room temperature. The solvents were removed under vacuum and the residue was dissolved in toluene, aided by sonication, and the solution Büchner filtered through a bed of Celite bed. The crude product was purified by preparative thin layer chromatography, eluting using dichloromethane and hexane (2:1). The desired product was obtained as a dark green crystalline solid (0.07 g, 75%). **IR** (solid, ATR): $\nu(\text{C}\equiv\text{C})$ 2117(br, w); $\nu(\text{C}=\text{O})$ 1690(s) cm⁻¹. **APCI-MS(+)**: m/z 558.2167 [(M+H)⁺ calculated 558.2168].

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

V. J. K. is supported by the Schlumberger Foundation Faculty for the Future program, and a Scholarship for International Research Fees from the University of Western Australia. This work was supported in part by the Australian Research Council through

the Discovery Program (DP190100073). We thank Dr Rebecca O. Fuller (University of Tasmania) for helpful discussions.

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