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Synthesis and characterization of new derivatives of azulene, including experimental and theoretical studies of electronic and spectroscopic behavior

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Four new azulene derivatives featuring two π -conjugated and sulfur terminated rigid side arms in the 1,3-positions of the azulene core were designed, synthesized, and characterized. The syntheses were carried out on the basis of a palladium cross-coupling procedure in the key reaction step. The crystal structures of the target compound 3 and of the intermediate compounds 7 and 9 have been studied. Supporting density functional theory calculations reveal insights into the electronic properties of the particular azulenes. The comparison of measured UV–Vis, infrared, and Raman data to calculated values allowed assignment of major spectral features to the particular structural differences of the new compounds and comparison to plain azulene. Cyclic voltammetry measurements were performed showing the redox characteristics of the new azulene derivatives. Copyright © 2012 John Wiley & Sons, Ltd. Supporting information may be found in the online version of this paper.

Keywords: azulene derivatives; cyclic voltammetry; DFT calculation; optical spectroscopy; single-crystal X-ray diffraction study

INTRODUCTION

The naphthalene isomer azulene is a blue nonbenzenoid aromatic hydrocarbon. Its small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap leads to remarkable electronic and optical properties, which result in potential applications in the fields of organic semicon-ductors,^[1,2] molecular switches,^[3,4] and organic photovoltaics.^[5,6] The ability to shift electronic density from the seven-membered ring toward the five-membered ring, which leads to a dipole moment of around 1.0D,^[7] is likely to stabilize cations as well as anions (Scheme 1). Hence, after single oxidation or reduction one ring of the radical ions maintains aromatic (cyclopentadienyl anion or tropylium cation). Furthermore, the radical in the other ring is mesomerically stabilized.

As indicated earlier, aromatic compounds and especially derivatives of azulene are possible candidates for molecular electronic devices.^[8] Following this line, a systematic approach to enable connection of the azulene to suitable electrodes in order to close the electric circuit between two electrodes and the azulene moiety might possibly be developed. This involves attachment of linear π -conjugated spacer units to the azulene with the spacers bearing specific end groups that show affinity to the electrode material. Because an electrode coated with gold was thought to be advisable, an end group comprising sulfur as the effective part for the contact was considered. However, it is known that current–voltage characteristics do not only depend on the molecular properties but also largely on the microscopic contact between the molecule and a metallic electrode.^[9] Hence, the decision was made to use aside from different spacers also

different types of sulfur-containing end groups in the structures of the molecules. Structures of the respective compounds together with a blueprint of their construction are illustrated in Scheme 2.

We report the synthesis of these new 1,3-disubstituted azulenes (1-4), show experimentally their properties in cyclic voltammetry (CV), UV–Vis and Raman spectroscopy, and discuss their behavior in these respects as compared with the results of corresponding density functional theory (DFT) calculations that have also been carried out including basic azulene. Moreover, the crystal structure of one of the target compounds (3) and two synthetic intermediates (7, 9) have been solved, giving indication of geometric parameters typical of the compound class.

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Scheme 1. Azulene and its stabilized single reduced and oxidized forms



Scheme 2. (a) Basic design of the studied compound type involving a connection of azulene (**A**), gold affine sticky end groups (**B**) and π -conjugated connection pieces (**C**). (b) Formula structures of the molecules **1–4**

EXPERIMENTAL

Methods and material

Melting points were determined with a Kofler melting point microscope and are uncorrected. The infrared (IR) measurements were carried out with a Nicolet-FT/IR-Spectrometer (Madison, WI, USA). The Raman measurements were performed at room temperature (rt) in backscattering geometry using a Labram HR 800 Horiba Jobin Yvon (Bensheim, Hessen, Germany) spectrometer with a charge-coupled device detector. As excitation wavelength, the 532-nm (2.33 eV) line of a frequency-doubled Nd:YAG laser was applied. In order to avoid thermal decomposition or laserinduced degradation of the specimen, the applied laser power density was carefully adjusted and kept very low (16 W cm⁻²). That is why acceptable Raman spectra were obtained within 10-20 min. Nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER (Billerica, Massachusetts, United States) AVANCE DPX 500 with tetramethylsilane as internal standard. For compound **1–4**, the ¹H and ¹³C Spectra can be found in the Supporting Information. The CV studies were carried out using a standard three-electrode setup: platinum working electrode, platinum counter electrode, and an Ag/ AgCl reference electrode. Anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate and 0.5 mM analyte was used. UV-Vis analyses were carried out with a JASCO (Groß-Umstadt, Hessen, Germany) V630 in dichloromethane. The liquid chromatography/mass spectrometry (MS) measurements were executed using a Varian (Böblingen, Baden-Württemberg, Germany) 3200Q-TRAP. For thin-layer chromatography analysis, aluminum sheets precoated with silica gel 60 F254 (Merck) (Darmstadt, Hessen, Germany) were used. Column chromatography was performed with silica gel (63–100 μ m, Merck). The solvents used were purified applying standard methods and for the coupling reactions degassed by ultrasonic treatment prior to use. Trimethylsilylethyne, triphenylphosphane, bis(triphenylphosphane)palladium(II) chloride, and copper(I) iodide were purchased from commercial sources.

Synthesis

The intermediate compounds 1,3-diiodoazulene (**5**),^{(6]} 3-ethynylthiophene (**6**),^{(10]} 3-[(4-ethynylphenyl)ethynyl]-thiophene (**7**),^[11] ethinylphenyl *tert*-butyl

sulfide (8),^[12] 1,3-bis[(trimethylsilyl)ethynyl]azulene (9),^[13] and 4-(acetylthio) iodobenzene (10),^[14] were prepared as described in the literature.

General procedure. Synthesis of compounds 1-3

1,3-Diiodoazulene (**5**) (0.60 g, 1.58 mmol), the respective ethynylic coupling component (3.47 mmol), bis(triphenylphosphane)palladium(II) chloride (50 mg, 0.07 mmol), copper(I) iodide (27 mg, 0.14 mmol) and triphenylphosphane (37 mg, 0.14 mmol) were dissolved in oxygen free diisopropylamine (50 mL) under an argon atmosphere. The solution (soln) was stirred at rt for 24 h and then at 50 °C for 10 h. After removal of the solvent, the residue was purified by column chromatography on SiO₂ to yield the pure products. Details for the individual compounds are given as follows.

1,3-Bis(3-thienylethynyl)azulene (1)

3-Ethynylthiophene (**6**) (0.38 g, 3.47 mmol) was reacted, and for chromatography, hexane–ethyl acetate 20:1 (v/v) was used as the eluent to yield 0.42 g (78%) dark green solid; mp = 120–122 °C; IR (KBr): v = 3104 cm⁻¹ (thiophene C–H), 2195 (C≡C), 1635, 1572, 1448, 1407, 1356, 862, 780, 748, 625; ¹H NMR (500 MHz, CDCl₃): δ = 7.26–7.31 (m, 4H, azulene–H and thiophene–H), 7.32 (dd, ³J_{HH} = 4.9 Hz, ⁴J_{HH} = 3.0 Hz, 2H, thiophene–H), 7.56 (dd, ⁴J_{HH} = 3.0 Hz, ⁴J_{HH} = 1.1 Hz, 2H, thiophene–H), 7.66 (t, ³J_{HH} = 9.9 Hz, 1H, azulene–H), 8.09 (s, 1H, azulene–H), 8.55 (d, ³J_{HH} = 9.3 Hz, 2H, azulene–H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ = 84.2 (C≡C), 88.9 (C≡C), 110.5, 122.8, 125.3, 125.5, 127.9, 129.9, 137.1, 140.0, 141.3, 141.8 ppm; MS (APCI): m/z = 341.1 [M + H]⁺ C₂₂H₁₂S₂ (340.04).

1,3-Bis{[4-(3-thienylethynyl)phenyl]ethynyl}azulene (2)

3-[(4-Ethynylphenyl)ethynyl]thiophene (**7**) (1.0 g, 4.80 mmol) was reacted and for chromatography hexane–ethyl acetate 2:1 (v/v) was used as the eluent to yield 0.54 g (63%) green solid; mp = 211 °C; IR (KBr): v = 3104 cm⁻¹ (thiophene C–H), 2189 (C≡C), 1568, 1527, 1486, 1445, 1363, 837 (ArC–H), 780, 742; ¹H NMR (500 MHz, CDCl₃) δ = 7.21 (dd, ³J_{HH} = 5.0 Hz, ⁴J_{HH} = 1.1 Hz, 2H, thiophene–H), 7.32 (dd, ³J_{HH} = 5.0 Hz, ⁴J_{HH} = 3.0 Hz, 2H, thiophene–H), 7.37 (t, ³J_{HH} = 9.9 Hz, 2H, azulene–H), 7.52 (d, ³J_{HH} = 8.4 Hz, 4H, Ar–H), 7.55 (dd, ⁴J_{HH} = 3.0 Hz, ⁴J_{HH} = 1.1 Hz, 2H, thiophene–H), 7.59 (d, ³J_{HH} = 8.4 Hz, 4H, Ar–H), 7.74 (t, ³J_{HH} = 9.9 Hz, 1H, azulene–H) pm; ¹³C NMR (125 MHz, CDCl₃) δ = 86.3 (C≡C), 86.8 (C≡C), 88.8 (C≡C), 94.1 (C≡C), 110.5, 122.1, 122.6, 123.6, 125.5, 126.0, 128.8, 129.8, 131.3, 131.5, 137.2, 140.2, 141.5, 142.1 ppm; MS (APCI): *m/z* = 540.2 [M]⁺ C₃₈H₂₀S₂ (540.10).

1,3-Bis[(4-tert-butylthiophenyl)ethynyl]azulene (3)

4-Ethinylphenyl *tert*-butyl sulfide (**8**) (0.66 g, 3.47 mmol) was reacted, and for chromatography, hexane was used as the eluent to yield 0.74 g (93%) dark green solid; mp = 102 °C; IR (KBr): $v = 2959 \text{ cm}^{-1}$ (CH₃), 2917, 2857, 2192 (C=C), 1572, 1363, 1477, 1435, 1394, 1166, 831; ¹H NMR (500 MHz, CDCI₃) $\delta = 1.32$ (s, 18H, CH₃), 7.35 (t, ³J_{HH} = 9.9 Hz, 2H, azulene–H), 7.56 (m, 8H, Ar–H), 7.73 (t, ³J_{HH} = 9.9 Hz, 1H, azulene–H), 8.14 (s, 1H, azulene–H), 8.61 (d, ³J_{HH} = 9.3 Hz, 2H, azulene–H) ppm; ¹³C NMR (125 MHz, CDCI₃) $\delta = 31.0$ (CH₃), 46.5 (C_{tert}), 86.4 (C=C), 93.7 (C=C), 110.5, 124.2, 125.9, 131.3, 132.8, 137.2, 137.3, 140.2, 141.6, 142.1; MS (ESI): m/z = 504.5 [M]⁺ C₃₄H₃₂S₂ (504.19).

1,3-Bis[(4-acetylthiophenyl)ethynyl]azulene (4)

The mixture of 1,3-bis[(trimethylsilyl)ethynyl]azulene (**9**) (0.93 g, 2.90 mmol) in methanol (50 mL) and potassium hydroxide (0.34 g, 6.0 mmol) in H₂O (6 mL) was stirred for 5 h at 0 °C. The soln is extracted three times with dichloromethane. The combined organic phases are washed with water and dried over Na₂SO₄. To the filtrate 4-(acetylthio) iodobenzene (**10**) (0.81 g, 2.91 mmol), bis(triphenylphosphane)palladium(II) chloride (31 mg, 0.04 mmol), copper(I) iodide (17 mg, 0.09 mmol), triphenylphosphane (23 mg, 0.09 mmol), and diisopropylamine (5 mL) are added, and the soln is stirred for 18 h at rt. The solvent is removed and

Crystallography

Crystals suitable for single-crystal X-ray diffraction studies were obtained by slow evaporation of soln of **3** (acetone) **9** (ether) and **11** (ether). Information concerning the crystallographic data and the structure refinement calculations of the three compounds is summarized in Table S1. The intensity data were collected on a Kappa/APEX II (Bruker AXS) diffractometer, with Mo K_x radiation (λ = 7.1073 nm) using ω and φ scans. Reflections were corrected for background, Lorentz, and polarization effects. Preliminary structure models were derived by application of direct methods^[15] and were refined by full-matrix least squares calculations on the basis of F^2 for all reflections.^[16] The hydrogen atoms were included in the models in the calculated positions and were refined as constrained to bonding atoms.

Electronic structure calculations

The DFT calculations on individual, free molecules were carried out by using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) program,^[17-23] which is an all-electron implementation of DFT. NRLMOL combines large Gaussian orbital basis sets, numerically precise variational integration and an analytic soln of Poisson's equation in order to accurately determine the self-consistent potentials, secular matrix, total energies, and Hellmann-Feynman-Pulay forces.^[24] The GGA/PBE^[25] functional was used to describe the exchange-correlation effects of the electrons. Because no structure data were available (except for compound ${\bf 3}),$ we generated starting geometries by ${\sf AVOGADRO},^{[26]}$ and geometry optimization was performed using the NRLMOL package. All results are based on these geometries. To improve the accuracy of the calculated spectroscopic properties, we utilized the ORCA^[27,28] program together with the B3LYP^[29,30] functional and the 6-31G*^[31] basis set. Note that the Fermi energy is defined similar to the standard definition of semiconductor physics within this paper as $E_{\rm F} = (E_{\rm LUMO} - E_{\rm HOMO})/2$.

RESULTS AND DISCUSSION

Structural design and synthesis of compounds

Considering the requirements stated at the beginning, the azulene-based target compounds (**1–4**) exhibit a specific connection mode of building units as shown in Scheme 2. This involves three structural components: (1) The azulene unit (**A**) as a redox element; (2) end groups (**B**) acting as alligator clips for the purpose of connecting to an electrode; and (3) rigid and π -conjugated pieces (**C**) combining the azulene with the end groups. These three parts were linked together using a process known as the Sonogashira–Hagihara cross-coupling^[32] as the key reaction step. Hence, corresponding aryl halides and terminal ethynes are the appropriate educts.

As specified in Scheme 3, 1,3-diiodoazulene (**5**) reacts with 3ethynylthiophene (**6**), 3-[(4-ethynylphenyl)ethynyl]-thiophene (**7**), or 4-ethinylphenyl *tert*-butyl sulfide (8) to yield **1**, **2**, and **3**, respectively. However, owing to problems in regard to the analogous coupling between **5** and 4-ethynyl(acetylthio)benzene for the synthesis of **4**, a different course was adopted by reaction of 1,3-diethynylazulene [via deprotection from 1,3-bis[(trimethylsilyl)



Scheme 3. Reaction scheme for the synthesis of 1, 2, and 3



Scheme 4. Reaction scheme for the synthesis of 4

ethynyl]azulene (9)] with 4-(acetylthio)iodobenzene (10) (Scheme 4). Nevertheless, this alternative coupling reaction gave only a moderate yield (15%) of 4, possibly attributable to the instability of the deprotected intermediate compound 1,3-diethynylazulene.

Crystal structures

Crystals suitable for X-ray diffraction analysis have been obtained for the intermediate compounds **7** and **9** as well as for the azulene derivative **3**. Crystal data for these compounds, structural features of the appertaining molecules, including torsion angles and selected bond lengths, and geometric parameters of possible intermolecular hydrogen bond type contacts are summarized in Tables S1–S2 (ESI), respectively. Further crystal data and geometric parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the reference numbers CCDC 826959, CCDC 826960, and CCDC 826961 for **9**, **3**, and **11**, respectively.

The yellow crystals of **7**, grown from soln in diethylether, show the monoclinic space group *Cc* with the asymmetric unit cell containing one molecule. The molecule deviates slightly from planarity, which is reflected by a twist angle of $2.9(1)^{\circ}$ between the aromatic rings [Fig. 1(a)]. Taking into account the dominant



Figure 1. (a) Molecular structure of **7** including the atom numbering scheme. Thermal displacement ellipsoids are drawn at 50% probability level. (b) Packing diagram of **7** viewed down the crystallographic *a*-axis

non-covalent interaction, the crystal of **7** can be regarded as being composed of molecular zigzag strands [Fig. 1(b)] in which consecutive molecules are connected by a relatively strong C– $H\cdots\pi$ hydrogen bond^[33] formed between the acidic ethynyl hydrogen and the thiophene ring [C1–H1…*ring center A* 26.6 nm, 161°]. Interstrand association is accomplished by $\pi\cdots\pi$ interactions^[34] between the phenylene and thiophene rings as well as weak C–H··· π contacts with the phenylene ring [C13–H13…*ring center B* 27.0 nm, 138°] and the terminal ethynyl unit [d(H··· π) 27.8–28.6 nm] acting as acceptors.

The azulene derivative **9** crystallizes as green rods in the monoclinic space group C2/c with one half of the molecule in the asymmetric entity of the unit cell. The molecule is situated on a crystallographic twofold axis passing through the atoms C1 and C6 [Fig. 2(a)]. The crystal structure of **9** is characterized by the formation of molecular stacks extending along the crystallographic *c*-axis [Fig. 2(b)]. Within a given stack, neighboring molecules are arranged in a head-to-tail fashion, which can be explained by the inherent dipole character of the azulene ring system. Because of the hydrophobic nature of the trimethylsilyl groups, the crystal structure is additionally stabilized by van der Waals forces.

Crystallization of **3** from acetone yields green crystals of the monoclinic space group *C*2/*c*. Because of packing effects, the planes of the azulene and phenylene units are considerably distorted against each other amounting to 56.16° and 60.19°, respectively, thus differing significantly from the expected planarity [Fig. 3(a)]. The molecules in the crystal of **3** are stacked along the *b*-axis, while the structure in the *a* and *c* direction is stabilized by C–H···π hydrogen bonding [C1–H1···*centroid*(C23/C24), 27.6 nm, 169.3°] and van der Waals interactions involving the *tert*-butyl group [Fig 3(b)].

Electronic properties

Density functional theory calculations for the basic azulene and the present derivates **1–4** were carried out to investigate the electronic structure of the molecules. Some fundamental properties such as HOMO–LUMO gap (HLG), Fermi level (E_F), the



Figure 2. (a) Molecular structure of **9** including the atom numbering scheme. Thermal displacement ellipsoids are drawn at 50% probability level. (b) Packing diagram of **9** viewed down the crystallographic *c*-axis

ionization potential (IP), and the electron affinity (E_{aff}) are summarized in Table 1. Figure 4 shows the calculated energy level diagrams together with plots of the HOMO and LUMO orbitals of the respective molecules.

In accordance to the literature,^[35,36] the HOMO (a 2a₂ state) and LUMO (a 4b₁ state) of azulene are ring-derived π -states. The calculated IP = 7.46 eV of azulene is in good agreement with the literature,^[37] whereas the calculated E_{aff} = 0.53 eV is about 30% too small compared with other calculations and experimental data.^[38,39] The attached linker units have the general effects of narrowing the HLG, increasing E_{aff} , and (slightly) decreasing the IP compared with the basic azulene. The position of the Fermi level is barely affected by the different linker units and remains at approx. $-3.7 (\pm 0.1)$ eV. The HOMO of the azulene derivatives is delocalized over the whole molecule, while the LUMO is always located at the azulene core. The latter effect is well known^[40] and results from the very low electron density at the substitution sites.

The structure of the density of states (DOS) around the Fermi level determines mainly the characteristics of the electron transport through a molecular device. Because of their very similar electronic properties, the DOS of the azulene derivatives are also very similar. Figure 5 shows the calculated DOS for compound **1**. The states below and above E_F are dominated by carbon π -states. Because of the integration of sulfur into the conjugated electronic system of the thiophene units, a small but reasonable amount of sulfur states can be found at the HOMO and the levels above the LUMO.





Az

4

2

2

1

3

Figure 3. (a) Molecular structure of **3** including the atom numbering scheme. Thermal displacement ellipsoids are drawn at 50% probability level. (b) Packing diagram of **3** viewed down the crystal-lographic *c*-axis

Table 1. Calculated	electronic properties of the different				
azulene compounds	(Fermi level, <i>E</i> _F ; HOMO–LUMO gap,				
HLG; electron affinity, E_{aff} ; ionization potential, IP)					

Compound	<i>E</i> _F [eV]	HLG [eV]	$E_{\rm aff}$ [eV]	IP [eV]	
Azulene	-3.74	3.24	-0.53	7.49	
	-3.78*	3.34*	-0.44*	7.16*	
1	-3.75	2.59	-1.27	6.21	
	-3.74*	2.65*	-1.23*	6.21*	
2	-3.69	2.38	-1.73	5.88	
	-3.65*	2.53*	-1.68*	5.99*	
3	-3.91	2.64	-1.50	6.15	
	-3.90*	2.79*	-1.48*	6.09*	
4	-3.89	2.63	-1.56	6.30	
	-3.87*	2.73*	-1.48*	6.28*	
Values marked with * are ORCA B3LYP results.					

Figure 4. Calculated energy level diagram aligned to E_F for compounds **1–4** and azulene (Az) free molecules. The molecular orbital density contours are depicted

With CV measurements, we are able to gain insights into the redox characteristics of the new azulene derivatives **1–4** compared with plain azulene. A voltammogram of **4** is exemplary illustrated in Fig. 6. The new compounds feature two oxidation and one reduction wave (Table 2), all being irreversible. A possible explanation is the dimerization in the 6-position of the azulene unit.^[41,42] Nevertheless, it is shown that the introduction of electron-withdrawing ethynylene groups to the azulene in the 1,3-positions leads to an increase of the oxidation potentials and the reduction potential. Because of the more extended π -conjugated system, compound **2** shows a smaller absolute value of E_{1}^{ex} and E_{1}^{red} , being in conformance with the trends of the calculated IP and E_{aff} .

UV–Vis spectroscopy

Figure 7 shows the measured UV–Vis spectra in dichloromethane of compounds **1** and **3** compared with reference measurement



Figure 5. Density of states (DOS) of **1** relative to the Fermi level E_F (red, total DOS; blue, carbon DOS; orange, sulfur DOS)



Figure 6. Cyclic voltammogram of 4 (0.5 mM) with scan rate of 25 mV/s

Table 2. Redox potentials of 1–4 and azulene measured by cyclic voltammetry, scan rate of 25 mV/s, V vs Ag/AgCl						
Compound	E_1^{ox} [V]	$E_2^{\rm ox}$ [V]	E_1^{red} [V]			
Azulene 1 2 3 4	0.67 0.92 0.79 0.94 0.97	1.33 1.83 1.73 1.67 1.80	-1.68 -1.28 -1.16 -1.21 -1.37			

of plain azulene. The narrowing of the HLG of **1** and **3** compared with azulene is qualitatively reflected by the shift of the weak HOMO–LUMO transition from 583 nm to approx. 630 nm. The typical HOMO–LUMO + 1 transition of azulene (340 nm) can be found at about 420 nm, which again reflects the calculated changes of the electronic properties (Table 1) by connecting the different side arms to the azulene core. The HOMO $1 \rightarrow$ LUMO transition is the most intensive band. For compound **1**, it can be found at 323 nm with an absorption coefficient of 1425 L mol⁻¹ cm⁻¹.



Figure 7. UV–Vis spectra of 1 and 3 compared with azulene. The spectra of 2 and looks very similar and are not shown for clarity

IR/Raman spectroscopy

Several investigations studying the vibrational properties of azulene by resonant Raman scattering were carried out in the past.^[43–45] FT-Raman and FT-IR spectra of the azulene single crystal in all possible polarizations at rt were reported by Bree *et al.*^[46] First calculations of the vibrational frequencies of azulene were presented by Steele.^[47] The work of Kozlowski *et al.*^[48] summarizes potential symmetry breaking as well as structure and definite vibrational assignment for azulene comparing both several numerical approaches and experimental results with each other.

Figure 8 shows the measured and DFT-calculated (shown are the results of the ORCA program together with the 6-31G* basis set and the B3LYP functional) IR spectra of the respective azulene derivatives. The main features are the strong C \equiv C signal (~2195 cm⁻¹), the C-H signal (~3104 cm⁻¹) originated by the thiophene linker (only **1** and **2**), and a large fingerprint region



Figure 8. Comparison of calculated (dashed) and measured (solid) infrared (IR) spectra of the investigated azulene compounds at room temperature. The intensities of the calculated spectra were scaled to match the measured ones

between 500 and 1500 cm⁻¹. The visible splitting of the C=C signal in **2** shows the two chemically different C=C bonds in the side arms. Further differences arise from the CH₃ (2923 cm⁻¹) groups (**3** and **4**) and the strong C=O (1698 cm⁻¹) stretching mode (**4**). The comparison of the calculated spectra to the measured data underpins the signal assignment. However, a clear resolution of the fingerprint area would need a far more detailed investigation. Although the positions of the main signals are in good agreement with the measured data, the respective intensities do not match very well.

The synthesized new azulene derivatives were examined by Raman spectroscopy at rt. Polarization-dependent measurements could not be carried out as no suitable single crystals of the samples were available. In Fig. 9, the obtained Raman spectra of the azulene derivatives are presented in the relevant spectral range. Obviously, the spectra were found to be very similar as one might expect because of only little structural differences of the linker groups. The results of *ab initio* calculations discussed earlier also predict only minor differences in the electronic properties of the azulene derivatives. The common Raman feature of all spectra at about 700 cm⁻¹ (marked as vib1) can be assigned as "breathing mode" (C–C stretch) of the seven-membered ring of the azulene crime of the azulene, this mode stays



Figure 9. Raman spectra of the investigated azulene derivatives recorded in backscattering geometry at room temperature (selected vibrations discussed explicitly in the text are depicted by the dashed lines)

unaffected, changing the substituent. Compared with that of plain azulene, the frequency of the considered Raman mode is blueshifted. The feature vib2 can be assigned to asymmetric C–C stretching of the seven-membered ring of the azulene core, which is only slightly affected by the attached linkers. The mode marked by vib3 is attributed to a C–C stretch vibration of the benzene ring of the substituents. Because of the lack of this structural feature in the linker group of compound **1** (Scheme 2), this mode cannot be observed in the respective Raman spectrum. Vib4 (~2200 cm⁻¹) can be assigned to the C=C triple bonds of the linker units. The measured and DFT calculated values of selected modes are collected in Table 3. The calculated values of the frequencies are slightly too high but a clear assignment to the measured modes can be made.

CONCLUSION

In summary, four new azulene-based compounds 1-4 featuring two π -conjugated side arms with different gold affine end groups have been synthesized and studied by means of singlecrystal X-ray diffraction, spectroscopic analysis, and CV, giving insight into their structural, vibrational, and electronic properties. Weak supramolecular interactions such as C–H··· π hydrogen bonding as well as $\pi \cdots \pi$ stacking interactions dominate the packing of the crystal structures. The experimental IR and Raman spectra of the target compounds together with the supporting DFT calculations ensure the success of the syntheses and are in good agreement with related literature data. The CV investigations of the azulenes in soln reveal that the radicals formed are likely to undergo consecutive reactions. The effects of the protection groups of compounds 3 and 4 are shown to be negligible in this regard, and one might also expect that the introduction of other sulfur end groups will not essentially change the electronic property of the molecule. This suggests that further tuning of the electronic property will require additional substitution to the azulene core including electron donor and acceptor groups both to the five-membered and seven-membered ring segments of the azulene as well as the fixation of a protection group to the 6-position of the azulene, preventing radical dimerization. Nevertheless, for an intended use of this type of compounds in a single molecule electronic device such as an electronic switching element between two gold electrodes, the stability of the radicals in the solid state is of more importance and remains to be investigated aside from the ability of the molecules regarding self-assembly to a gold surface. These are the tasks we are concerned with in the near future.

Table 3. Measured and calculated values (cm ⁻¹) of selected spectral features								
Compound	Raman							
	Vib1		Vib2		Vib3		Vib4	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
1	720	700	1648	1570	_	_	2318	2197
2	715	700	1646	1573	1663	1598	2304	2188
3	720	700	1645	1572	1646	1590	2311	2200
4	720	700	1645	1575	1648	1592	2311	2197

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