First π-linker featuring mercapto and isocyano anchoring groups within the same molecule: synthesis, heterobimetallic complexation and self-assembly on Au(111)

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Mercapto (–SH) and isocyanato (–N==C) terminated conducting π-linkers are often employed in the ever-growing quest for organoelectronic materials. While such systems typically involve symmetric dimercapto or disiocyanato anchoring of the organic bridge, this article introduces the chemistry of a linear azulenic π-linker equipped with one mercapto and one isocyano terminus. The 2-isocyanato-6-mercaptoazulene platform was efficiently accessed from 2-amino-6-bromo-1,3-dithioethercarbonylazulene in four steps. The 2-N==C end of this 2,6-azulenic motif was anchored to the [Cr(CO)5] fragment prior to formation of its 6-SH terminal. Metalation of the 6-SH end of [(OC)5Cr(N==C-1,3-dithioethercarbonyl-6-mercaptoazulene)] with PPh3AuCl under basic conditions, afforded X-ray structurally characterized heterobimetallic C/C/AuI ensemble [(OC)5Cr(N==C-1,3-dithioethercarbonyl-6-mercaptoazulene)]AuPPh3 under basic conditions, [(OC)5Cr(N==C-1,3-dithioethercarbonyl-6-mercaptoazulene)]AuPPh3 (8). Analysis of the 13C NMR chemical shifts for the [(NC)Cr(CO)5] core in a series of the related complexes [(OC)5Cr(N==C-6-X-1,3-dithioethercarbonylazulene)] (X = N==C, Br, H, SH, CH2CH2CO2CH2CH2S, SPh3PPh2) unveiled remarkably consistent inverse-linear correlations Δ(13COCO) vs. Δ(13C-CN) and Δ(13CCOS) vs. Δ(13CN) that appear to hold well beyond the above 2-isocyanaoazulenic series to include complexes [(OC)5Cr(NCN)] containing strongly electron-withdrawing substituents R, such as CF3, CFCF2Cl, CCl3F, and C6F5. In addition to functioning as a sensitive 13C NMR handle, the essentially C₆₀-symmetric [1–(NC)Cr(CO)₅] moiety proved to be an informative, remote, ν₁=κ=κ₁ infrared reporter in probing chemosorption of 7 on the Au(111) surface.

Introduction

Mercapto (–SH) and isocyanato (–N==C) substituents are among particularly popular anchoring groups in coordination and surface chemistry as they are well-known to provide stable junctions at metal/organic interfaces.4–9 Even though dimercapto- and disiocyanato-functionalized molecular linkers have long been attracting interest of theorists4–9 and experimentalists10–15 in the quest for efficient organoelectronic materials,16–20 species containing both –SH and –N==C functionalities in the same molecule are not presently known and constitute a formidable synthetic challenge. Indeed, a mercapto group is incompatible with reaction conditions commonly employed to form an isocyanato substituent,24 whereas free organic isocyanides are unlikely to tolerate chemical environments typically involved in the syntheses of mercaptans (thiols).23–24 In the context of targeting isocyanothiols for bridging metal-based electron reservoirs, a potentially straightforward strategy to circumvent the above dilemma would be to anchor either the –N==C or the –SH terminus of such a hypothetical linker prior to forming and tethering its other end. There is only one related example in the literature, albeit not involving a mercapto group per se but rather its disulfide surrogate.25,26 In their elegant approach to covalently bind nickel clusters to a gold surface via the 4-isocyanophenylthiolate bridge, Kubiak and coworkers attached both –N==C ends of otherwise non-isolable 1,2-bis[4-isocyanophenyl]disulfide to trinuclear nickel clusters in the μ₃-η¹ fashion.25 The resulting salt, [(μ₃-I)2(μ₂-dppm)3(μ₃-η¹-C₆H₅S)2]2+ (dppm = bis(diphenylphosphino)methane), underwent homolysis of its S–S moiety upon exposure to a gold surface to give rectifying, presumably ionic, monolayer films.26
Earlier this year, Ratner and van Dyck proposed a new paradigm for the design of efficient molecular rectifiers that involved two \( \pi \)-conjugated units asymmetrically anchored to metallic electrodes and separated by a decoupling bridge.\(^{27}\) Their intriguing theoretical study suggested mercapto and cyano (\(-\text{C} \equiv \text{N}\)) junctions for accommodating the asymmetric anchoring on the premises that the \(-\text{SH}\) and \(-\text{C} \equiv \text{N}\) termini would facilitate alignments of a linker’s HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), respectively, through Fermi level pinning.\(^{37}\) We note that, from a practical standpoint, mercapto/isocyano asymmetric anchoring would be worth considering as well, given that the isocyano group offers a substantially more stable junction within a wider range of organometallic platforms compared to its isomeric cyano congener.\(^{2}\)

Herein, we introduce chemistry of the first, to the best of our knowledge, \( \pi \)-linker equipped with mercapto and isocyano anchoring groups. The linker’s core is comprised of the non-alternant aromatic framework of azulene, a substitution-free molecular diode which has, among other unusual physico-chemical characteristics, complementary orbital density distributions within its Frontier molecular orbitals (Fig. 1).\(^{28}\)

**Results and discussion**

Recent synthetic breakthroughs in functionalization of the azulenic scaffold along its molecular axis have expanded the toolbox for developing low band-gap conducting and optoelectronic materials.\(^{29-32}\) The design of the title \( \pi \)-conjugated linker was influenced by and capitalized on our earlier studies involving 2,6-diisocyano- and 2,6-dimercapto-1,3-dithiocarbonylazulenyls, shown in Fig. 2 (compounds 1 and 2, respectively). As illustrated in Fig. 2, one can envision pursuing two hybrids of 1 and 2: 2-isocyano-6-mercapto-1,3-dithiocarbonylazulene (3a) and 2-mercapto-6-isocyano-1,3-dithio-carbonylazulene (3b). Among these two hybrids, 3a is particularly interesting because each substituent in its structure reinforces the molecular dipole of the azulenic framework. In fact, our Density Functional Theory (DFT) calculations suggest that the dipole moment of the “parent” azulene molecule should increase nearly 10-fold upon incorporation of all substituents to form 3a (Fig. 3).

Our synthetic approach to constructing and metalating 3a is shown in Scheme 1. Treating pink 2-formamido-6-bromo-1,3-diethoxycarbonylazulene\(^{32,34}\) with ethyl 3-mercapto-propionate in refluxing pyridine afforded persimmon-coloured thioether 4 in a high yield. Dehydrating the 2-formamido group of 4 cleanly provided peach-red 2-isocyanoazulene derivative 5. Unlike 1,2-bis(4-isocyanophenyl)disulphide (vide supra),\(^{27,29}\) 5 is thermally and air-stable for practical purposes and can be stored under ambient conditions for at least a few weeks without spectroscopically \( ^1 \text{H NMR, FTIR} \) detectable deterioration. Compound 5 reacted with \( \text{Cr(CO)}_5(\text{THF}) \) via its 2-NC end to form orange \( \text{Cr}^{0} \) adduct 6. No product featuring the thioether S–P unit in its structure was isolated, presumably due to the symmetric nature of its S–S bonds. Metalation of the 6-SH end of 7 with \( \text{PPh}_3\text{AuCl} \) under basic conditions yielded orange-red crystals of heterobimetallic \( \text{Cr}^0/\text{Au}^1 \) complex 8 after a simple workup.

The solid-state structure of \( 8 \) features two very similar but crystallographically independent molecules of 8 in the asymmetric unit that are linked together via a weak Au···Au interaction\(^{39}\) of 3.2102(4) Å (Fig. 4, 5, S3 and S4†). The partially positively charged 7-membered ring of the highly polarizable azulenic moiety in each of these molecules of 8 undergoes donor–acceptor face-centred stacking\(^{37}\) with a Ph-ring of the other molecule’s \( \text{PPh}_3 \) ligand giving the intercentroid distances\(^{40}\) of 3.65 and 3.76 Å. Heterobimetallic complex 8 may be viewed as a hybrid of our X-ray structurally characterized mononuclear \( \text{Cr}^{10} \) and \( \text{Au}^1 \) adducts of 1 and 2, respectively, depicted in Fig. 6 (complexes 9 (ref. 32) and 10 (ref. 29)). While the S-Au-P unit in 10 is practically linear (ca. 177.4°),\(^{29,39}\) bending of the S–Au–P angle (ca. 166.5°) in 8 is undoubtedly a consequence of the Au···Au bonding reinforced further by the

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**Fig. 1** (a) Polar resonance form of azulene and C-atom numbering scheme of the azulenic scaffold; (b) Frontier molecular orbitals of azulene.

**Fig. 2** 2,6-Diisocyano-1,3-diethoxycarbonylazulene (1),\(^{32} \) 2,6-dimercapto-1,3-diethoxy-carbonylazulene (2),\(^{29} \) and their hypothetical hybrids 3a and 3b.

**Fig. 3** DFT-calculated electric dipole moments (in Debye) of azulene and its derivatives.
“aromatic donor-acceptor interactions”. The above structural perturbations do not significantly affect the Au–S–C angle in 8 compared to that in 10, which are ca. 107.8° and 105.0°, respectively. Notably, the solid state structure of 10 exhibits neither aurophilic nor aromatic stacking interactions akin to those observed.

The metric parameters for the octahedral \([\text{(-NC)}\text{Cr(CO)}_5]\) core in 8 are quite similar to those observed for 9 (ref. 32) and many other complexes (ArylNC)Cr(CO)_5. Comparison of the Cr–CN and C≡N bond distances for 8 and 9 (Table 1) may hint that the 2-isocyanoazulene ligand in 8 has a somewhat higher σ-donor/π-acceptor ratio than that in 9, thereby reflecting the difference in electron-donating/withdrawing characteristics of −SAuPPh_3 versus −N≡C groups at position 6 of the azulenic scaffold. However, this suggestion should be taken cum grano salis as such subtle variations in d(Cr–CN) and d(C≡N) are statistically ambiguous, especially under the 3σ criterion. More drastic changes in the electronic nature of the isocyanide ligand’s substituent do lead to significant alterations in the Cr–CN and C≡N bond lengths in (RNC)Cr(CO)_5 as illustrated in Table 1 for R = Bu (ref. 42) and FC≡CF_2.

Compounds 4–8 are highly coloured substances. The lowest energy electronic absorption band for 5 occurs at 484 nm (ε = 1.55 × 10^3 M⁻¹ cm⁻¹) and is 259 cm⁻¹ red-shifted compared to the S0 → S1 transition documented for 4 (Fig. S1†). This red shift arises from the greater electron-withdrawing influence of the 2-isocyano group in 5 versus the 2-formamido group in 4 on the energy of the azulenic scaffold’s LUMO (Fig. 1b). The UV-vis spectra of 6 and 7 are nearly identical and feature very intense absorption bands at 454 (ε = 3.1 × 10^4 M⁻¹ cm⁻¹) and 452 (ε = 2.6 × 10^4 M⁻¹ cm⁻¹), respectively, that have a substantial contribution from the dπ(Cr) → π*([CNAzulenyl]) charge transfer (Fig. 7 and S1†). Our time-dependent DFT (TD-DFT) calculations for 7 suggest that the transition at 452 nm (TD-DFT: 416 nm) has 85% HOMO → LUMO character (Fig. 8a).

Upon metatation of 7 to form 8, this band not only red-shifts to 469 nm (TD-DFT: 463 nm for 8a, the truncated model of 8 featuring OMe and PMe_3 groups instead of OEt and PPh_3, respectively, Fig. 8b) but also more than doubles in intensity (ε = 5.4 × 10^4 M⁻¹ cm⁻¹). This intensity gain is due to the addition of the n(S) → π*([CNAzulenyl]) character to the HOMO → LUMO transition observed for 8 (cf. the 445 nm band for 10 in Fig. 7). As in the case of 9 and 10, the LUMOs of 7 and 8a constitute the π*-system of the azulenic moiety with contributions from both anchoring groups while their HOMOs involve the entire 2-isocyano-6-azulenylthiolate motif (Fig. 8).

Whilst considering 13C NMR signatures of the [NC]Cr(CO)_5 core in 6, 7, 8, and 9, we noticed that they were predictably sensitive to the nature of the substituent at position 6 of the azulenic scaffold. To further validate this initial observation, we
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Table 1 Selected bond distances and angles for 8, 9, and (RNC)Cr(CO)3 (R = Bu, C2F3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>D(Cr-CN), Å</th>
<th>D(C=N), Å</th>
<th>θ (C-N-C), °</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BuNC)Cr(CO)3</td>
<td>2.016(2)</td>
<td>1.150(2)</td>
<td>177.9(2)</td>
</tr>
<tr>
<td>8a</td>
<td>1.960(6)</td>
<td>1.135(7)</td>
<td>172.6(6)</td>
</tr>
<tr>
<td>8b</td>
<td>1.969(5)</td>
<td>1.138(6)</td>
<td>173.3(5)</td>
</tr>
<tr>
<td>9c</td>
<td>1.953(4)</td>
<td>1.166(4)</td>
<td>167.5(3)</td>
</tr>
<tr>
<td>(F3C2NC)Cr(CO)3</td>
<td>1.909(2)</td>
<td>1.162(2)</td>
<td>173.6(2)</td>
</tr>
</tbody>
</table>

a Data for two crystallographically unique molecules. b Ref. 41.

The top six rows in Table 2 contain 13C NMR data pertaining to the [(NC)Cr(CO)3] moiety in this series of six 2-isocyanoazulenic adducts. All of these 13C NMR measurements were performed for samples dissolved in CDCl3.

From Table 2 it is evident that as the net electron-releasing ability of X decreases (SAuPPh3 > SCH2CH2CO2CH2CH3 > SH > H > Br > N≡C), the δ(13CN) value for the isocyano carbon resonance increases in the range spanning ca. 8 ppm, thereby signifying gradual drop in the σ-donor/π-acceptor ratio of the 2-isocyano-6-X-azulene ligand. Concomitantly, both δ(13COtrans) and δ(13COcis) values decrease, albeit in tighter chemical shift ranges (~1.0 and ~0.5 ppm, respectively), indicating reduction in the electron richness of the Cr-centre. Even though the 13C chemical shifts of terminal CO and CNR ligands in low-valent complexes are influenced considerably by the paramagnetic shielding term, δPAR, which reflects the degree of π-backbonding, it is more appropriate to interpret Δδ(13CN) and Δδ(13CO) as a combined σ-donor/π-acceptor effect.

Closer examination of the 13C NMR data in the top six rows of Table 2 unveiled remarkably consistent inverse-linear relationships δ(13COtrans) vs. δ(13CN) and δ(13COcis) vs. δ(13CN), as illustrated in Fig. 9. This figure also confirms that remote modulation the Cr-centre’s electron richness mediated by the 2,6-azulenic framework affects the trans-CO ligand to a greater extent than the cis-CO’s of the [(NC)Cr(CO)3] moiety. Would the trends depicted in Fig. 9 hold beyond the 2-isocyanoazulenic series? To address this question, we considered (RNC)Cr(CO)5 species containing strongly electron-withdrawing substituents R, for which 13C NMR data acquired in the same solvent (CDCl3) were available (bottom four rows in Table 2). The expanded δ(13COtrans) vs. δ(13CN) and δ(13COcis) vs. δ(13CN) plots that, in

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(13CN)</th>
<th>δ(13COtrans)</th>
<th>δ(13COcis)</th>
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</thead>
<tbody>
<tr>
<td>Ph3PAuS</td>
<td>178.55</td>
<td>217.26</td>
<td>214.91</td>
</tr>
<tr>
<td>O3C(CH2CH3)</td>
<td>218.72</td>
<td>216.85</td>
<td>214.68</td>
</tr>
<tr>
<td>(BuNC)Cr(CO)3</td>
<td>182.27</td>
<td>216.77</td>
<td>214.65</td>
</tr>
<tr>
<td>(F3C2NC)Cr(CO)3</td>
<td>186.6</td>
<td>216.3</td>
<td>214.4</td>
</tr>
<tr>
<td>8a</td>
<td>193.8</td>
<td>214.6</td>
<td>213.3</td>
</tr>
<tr>
<td>8b</td>
<td>199.3</td>
<td>214.2</td>
<td>213.0</td>
</tr>
<tr>
<td>9c</td>
<td>208.2</td>
<td>212.0</td>
<td>212.0</td>
</tr>
<tr>
<td>Ref. 32.</td>
<td>211.1</td>
<td>211.5</td>
<td>211.7</td>
</tr>
</tbody>
</table>

a All spectra were recorded in CDCl3. b Ref. 32. c Ref. 47. d Ref. 43. e Ref. 48.
addition to the 2-isocyanoazulene complexes, include (OC)5-Cr(CNR) with R = C6F5, C2F5, CFClCF2Cl,43 and CF3 (ref. 48) are shown in Fig. 10, which again demonstrates excellent inverse-linear correlations now spanning substantially wider \( \Delta \delta^{(13}CN) \) and \( \Delta \delta^{(13}CO) \) windows.

The above \( \delta^{(13}CO)/\delta^{(13}CN) \) NMR analysis serves as a convenient tool for quantifying even subtle electronic influence of a CNR ligand’s substituent R. In this regard, it offers a simple alternative to the well-established method involving correlation the carbonyl \( ^{13}C \) chemical shifts with the corresponding CO force constants \( k_{CO} \) for complexes (RNC)Cr(CO)5.40,49,50 Unfortunately, changes in \( k_{CO} \) due to mild electronic perturbations of the R group are often not clearly discernible.40,51 Determining the values of \( k_{CO} \)’s under the C_{av} symmetry for complexes (RNC)Cr(CO)5 using the Cotton–Kraihanzel (C-K) approximation is a straightforward but somewhat tedious task that carries fundamental limitations and relies on the availability of the complete \( v_{c=o} \) vibrational profile\(^{52-54} \) (\( v_{c=o} = 2A_1 + B_1 + E \), e.g., Fig. 11 (ref. 55 and 56) and Table S17). In the IR spectra of LM(CO)5 species, the lower energy \( v_{c=o}(A_1) \) band is often obscured by the intense \( v_{c=o}(E) \) band,\(^{53-54} \) which compromises the accuracy of experimental determination of this \( v_{c=o}(A_1) \) value (vide infra).

Similar to the trend in \( \delta^{(13}CN) \) for the (RNC)Cr(CO)5 adducts in Table 2, the \( ^{13}C \) NMR resonance for the terminal C-atom in the available uncoordinated 2-isocyanoazulenes moves upward upon increasing electron-donating power of the substituent X at the azulene 6-position \( (\delta = 179.9, 178.0, 177.5, 176.3 \text{ ppm in CDCl}_3 \text{ for X = } \equiv \text{C}, \text{Br}, \text{H}, \text{SCH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3, \text{respectively}) \). Yet, the \( \delta_{X=c=o} \) stretching frequency for these free 2-isocyanoazulenes \( (2126 \pm 1 \text{ cm}^{-1} \text{ in } \text{CH}_2\text{Cl}_2) \) is insensitive to the nature of the group X. However, upon proceeding from 8 to (6, 7, 11) to 12 to 9, the \( \delta_{X=c=o} \) band undergoes a small red shift (Table 3), thereby suggesting decrease in the \( o\)-donor/\( \pi\)-acid ratio of the isocyano ligand, especially when 8 is compared to 9 and 12.

Fig. 12a shows the FTIR spectrum of thiol 7 in CH2Cl2. In addition to the characteristic \( v_{p-H} \) and \( v_{p=N-C} \) bands at 2583 and 2140 cm\(^{-1} \), respectively, it features a typical pattern in the \( v_{c=o} \) stretching region for a LM(CO)5 species. The band at 2049 cm\(^{-1} \) corresponds to the \( v_{c=o} \) mode \( A_1^{(1)} \) where all five CO

Fig. 10 (a) Plot of \( \delta^{(13}CO_{trans}) \) vs. \( \delta^{(13}CN \) chemical shifts (in CDCl3) in the \( ^{13}C \) NMR spectra of all compounds from Table 2, (b) plot of \( \delta^{(13}CO_{cis}) \) vs. \( \delta^{(13}CN \) chemical shifts (in CDCl3) in the \( ^{13}C \) NMR spectra of all compounds from Table 2.

Fig. 11 DFT-calculated \( v_{c=o} \) vibrational profile for (MeNC)Cr(CO)5 in the gas phase.\(^{55,56} \)
ligands vibrate in-phase (cf. Fig. 11). The very weak band at 2000 cm\(^{-1}\) is due to the \(v_{C=O}\) vibration of \(B_1\)-symmetry, which is IR-forbidden under the strict \(C_{4v}\) symmetry but gains slight intensity because of minor deviations of the structure from the idealized \(C_{4v}\) geometry. The intense \(v_{C=O}\) band at 1958 cm\(^{-1}\) chiefly represents the doubly degenerate vibration of \(E\)-symmetry. This \(v_{C=O}\) (\(E\)) mode obscures the remaining IR-active \(v_{C=O}\) mode \(A_1^{(2)}\) (2). Interestingly, perturbations of the local \(C_{4v}\) symmetry in 7 through crystal packing interactions in the solid state are sufficient to split the \(E\)-mode into two separate \(v_{C=O}\) peaks while unmasking the original \(A_1^{(2)}\) mode (Fig. 12b).

Exposing ca. 1 × 1 cm\(^2\) gold substrates to a 2 mM solution of 7 in CHCl\(_3\) without protection from air and ambient lighting reproducibly afforded self-assembled monolayer (SAM) films of 7 on the Au(111) surface. This chemisorption process is presumably accompanied by formation of the thiolate junction and the release of H\(_2\). The reflection absorption infrared (RAIR) spectrum of the SAM of 7 on Au(111) is shown in Fig. 13a.

Our optical ellipsometry measurements on multiple SAMs of benzenoid mercaptoazulenes on Au(111) can be highly variable.\(^{67}\) We have recently shown that 2-mercaptoazulene and several of its derivatives form monolayer films on Au(111) with approximately upright assembly of the azulenythiolate constituents.\(^{63}\)

Our optical ellipsometry measurements on multiple SAM samples of 7 provided consistent SAM thickness values that nicely corroborate the monolayer nature of these films and upright orientation of the molecules on the gold surface (Table 4). In terms of their composition, the SAMs of 7 and 9 on Au(111) differ only in the surface anchoring group (thiolate vs. isocyanide) and appear to exhibit essentially identical thicknesses.\(^{64}\) Notably, neither RAIR spectroscopic nor ellipsometric data collected for the SAMs of 7 on Au(111) would be consistent with such an idealized arrangement due to the very weak band at 2000 cm\(^{-1}\), which is a consequence of the IR-forbidden nature of the \(A_1\) vibrations in the gas phase. However, the intense band at 2058 cm\(^{-1}\) in the RAIR spectrum of 7 is consistent with the \(E\)-mode, which is IR-active due to the axial \(B_1\) vibrations of the \([\text{Cr(CO)}_5]\) unit. The \(A_1^{(1)}\) and \(A_1^{(2)}\) bands at 2058 and 1995 cm\(^{-1}\) in the RAIR spectrum in Fig. 11 both exhibit significant blue shifts compared to the corresponding \(v_{C=O}\) peaks in the solution FTIR spectrum of 7 (2049 and 1958 cm\(^{-1}\), respectively, Fig. 10a). The magnitudes of these shifts appear to be too high, especially in the case of the \(A_1^{(2)}\) mode, to be attributed solely to differences in intermolecular interactions within the SAM vs. solution of 7. The larger change in energy of the \(v_{C=O}\) \(A_1^{(2)}\) mode compared to that of the \(A_1^{(1)}\) mode upon chemisorption of 7 stems from the greater contribution of the \(trans\)-CO stretch to the former.\(^{62}\)

The tilt angle of the aromatic moiety in SAMs of benzenoid mercaptoazulenes on Au(111) can be highly variable.\(^{67}\) We have recently shown that 2-mercaptoazulene and several of its derivatives form monolayer films on Au(111) with approximately upright assembly of the azulenythiolate constituents.\(^{63}\)
Cr(CO)\textsubscript{5} moiety served as a distinctly informative unit rather than focusing on the [Cr(CO)\textsubscript{5}] fragment in the thicknesses (in \textm{\AA}) of the SAMs of 7, 6-mercaptopo-1,3-diethoxycarbonylazulene, and 6-mercaptopo-2-chloro-1,3-diethoxycarbonylazulene

<table>
<thead>
<tr>
<th>Mercaptoazulene derivative</th>
<th>(D_{\text{obs}}^a)</th>
<th>(D_{\text{calc}}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>18.3 ± 2.7</td>
<td>17.1</td>
</tr>
<tr>
<td>6-Mercapto-1,3-diethoxycarbonylazulene</td>
<td>12.8 ± 1.9</td>
<td>13.3</td>
</tr>
<tr>
<td>6-Mercapto-2-chloro-1,3-diethoxycarbonylazulene</td>
<td>14.6 ± 1.9</td>
<td>13.3</td>
</tr>
</tbody>
</table>

\(^a\) Average of five measurements at different spots on multiple SAM samples. \(^b\) Calculated from the X-ray structural data for 8, 6-mercapto-1,3-diethoxycarbonylazulene [ref. 29], and 6-mercapto-2-chloro-1,3-diethoxycarbonylazulene [ref. 29], as well as by assuming straight C–S–Au\textsubscript{surface} angle and the Au(111)–S distance of 2.45 \textm{\AA} (ref. 58).

with the “on-top-bent”\textsuperscript{39} or any other adsorption models of 7 invoking a bent C–S–Au\textsubscript{surface} geometry. The ellipsometric measurements on SAM films formed from our recently reported\textsuperscript{39} 6-mercapto-1,3-diethoxycarbonyl-azulene and 6-mercapto-2-chloro-1,3-diethoxycarbonylazulene also corroborate that these 6-mercaptoazulenes self-assemble on Au(111) surfaces in the upright fashion (Table 4).

**Conclusions**

The asymmetric nonbenzenoid aromatic framework of azulene proved to be a convenient platform for accessing the first \(\pi\)-linker terminated with both mercapto and isocyanato junction moieties. Anchoring the 2-isocyano end of this linker was an important prerequisite to successfully installing its 6-mercapto terminus. The \(^{13}\text{C}\) NMR signatures of the octahedral [\(\square\text{NCr(CO)}\text{\textsubscript{5}}\)] core in related complexes 6, 7, 8, 9, 11, and 12 provided a sensitive spectroscopic handle for tuning electron richness of the \(\text{Cr}\text{\textsuperscript{0}}\)-centre through mediation by the 2,6-azulenic frame

**Notes and references**


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39 Average value for two crystallographically unique molecules.
41 The differences in Cr=CO\text{trans}, C≡O\text{trans} average Cr=CO\text{cis}, and average C≡O\text{cis} bond lengths in 8 and 9 are insignificant.
42 W. Sattler and G. Parkin, Chem. Commun., 2009, 7566 and CCDC # 744953†
55 Calculations performed at the BP86/TZVP level. For a similar analysis at the BP86/DZP level originally reported by King, et al., see: J. Wang, G. Li, Q. Li, Y. Xie and R. B. King, Polyhedron, 2012, 47, 165.