First \(\pi\)-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 isocyano (–N≡C) terminated conducting \(\pi\)-linkers are often employed in the ever-growing quest for organoelectronic materials. While such systems typically involve symmetric dimercapto or disiocyno anchoring of the organic bridge, this article introduces the chemistry of a linear azulenic \(\pi\)-linker equipped with one mercapto and one isocyano terminus. The 2-isocyano-6-mercaptaoazulene platform was efficiently accessed from 2-amino-6-bromo-1,3-diethoxy carbonyl azulene 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 terminus. Metalation of the 6-SH end of [[OC]\(_5\)Cr(\(\eta^1\)-2-isocyano-1,3-diethoxy carbonyl-6-mercaptaoazulene)](7) with \(\text{Ph}_3\text{P}\text{AuCl}\) under basic conditions, afforded X-ray structurally characterized heterobimetallic \(\text{Cr}^0/\text{Au}^+\) ensemble [[OC]\(_5\)Cr(\(\eta^1\)-\(\eta^1\)-2-isocyano-1,3-diethoxy carbonyl-6-azulenylthiolate)AuPPh\(_3\)](8). Analysis of the \(^{13}\text{C}\) NMR chemical shifts for the [[(NC)\(_2\)Cr(CO)\(_5\)] core in a series of the related complexes [[OC]\(_5\)Cr(2-isocyano-6-X-1,3-diethoxy carbonyl-azulene)](X = \(\text{N}-\text{C}^\equiv\text{C}\), Br, H, \(\text{SCH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3\), \(\text{SAuPPh}_3\)] unveiled remarkably consistent inverse-linear correlations \(\delta\)\(^{13}\text{CO}_{\text{vide}}\) vs. \(\delta\)\(^{13}\text{CN}\) and \(\delta\)\(^{13}\text{CO}_{\text{vide}}\) vs. \(\delta\)\(^{13}\text{CN}\) that appear to hold well beyond the above 2-isocyanoazulenic series to include complexes [[OC]\(_5\)Cr(CN)R] containing strongly electron-withdrawing substituents R, such as CF\(_3\), CF\(_2\)Cl, C\(_2\)F\(_5\), and C\(_6\)F\(_5\). In addition to functioning as a sensitive \(^{13}\text{C}\) NMR handle, the essentially \(\text{C}_\text{d}_{6v}\)-symmetric [[(–N\(\equiv\text{C}^\equiv\text{C})\text{Cr}^0(\text{CO})\(_5\)] moiety proved to be an informative, remote, \(\eta^1\)-\(\eta^1\)-infrared reporter in probing chemisorption of 7 on the Au(111) surface.

Introduction

Mercapto (–SH) and isocyano (–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.\(^5\)\(^–\)\(^9\) Even though dimercapto- and disiocyno-functionalized molecular linkers have long been attracting interest of theorists\(^1\)\(^–\)\(^3\) and experimentalists\(^10\)\(^–\)\(^15\) 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 isocyano substituent,\(^21\)\(^–\)\(^24\) whereas free organic isocyanides are unlikely to tolerate chemical environments typically involved in the syntheses of mercaptans (thiols).\(^25\)\(^–\)\(^28\) 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-isocyanothiophosphine bridge, Kubiak and coworkers attached both –N≡C ends of otherwise non-isolable 1,2-bis(4-isocyano) disulfide to trinuclear nickel clusters in a \(\mu_3\)-\(\eta^1\)-fashion.\(^25\) The resulting salt, \([\text{Ni}_3(\mu_3\text{I})(\mu_2\text{dpmm})(\mu_3\text{S})\text{C}(\text{CN})\text{NH}_3\text{H}_2\text{S}^-]_{\text{Li}}\text{dpmm = bis(diphenylphosphino)methane}\), underwent homolysis of its S–S moiety upon exposure to a gold surface to give rectifying, presumably ionic, monolayer films.\(^26\)
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. The design of the title π-conjugated linker was influenced by and capitalized on our earlier studies involving 2,6-diisocyano- and 2,6-dimercapto-1,3-diethoxycarbonylazulenes, 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-isocyanato-6-mercaptop-1,3-diethoxycarbonylazulene (3a) and 2-mercaptop-6-isocyanato-1,3-diethoxycarbonylazulene (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 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 with ethyl 3-mercaptopropionate 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), 5 is thermally and air-stable for practical purposes and can be stored under ambient conditions for at least a few weeks without spectroscopically (1H NMR, FTIR) detectable deterioration. Compound 5 reacted with Cr(CO)₅(THF) via its 2-NC end to form orange Cr₃ adduct 6. No product featuring the thioether S/C₇ backbone was formed. Metalation of the 6-SH end of 7 with PPh₃·AuCl under basic conditions yielded orange-red crystals of heterobimetallic Cr₄/Au复合物 8 after a simple workup.

The solid-state structure of 8-CH₂Cl₂ features two very similar but crystallographically independent molecules of 8 in the asymmetric unit that are linked together via a weak Au···Au interaction of 3.2102(4) Å. 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 with a Ph-ring of the other molecule’s PPh₃ ligand giving the intercentroid distances of 3.65 and 3.76 Å. Heterobimetallic complex 8 may be viewed as a hybrid of our X-ray structurally characterized mononuclear Cr(CO)₅ and Au(I) adducts of 1 and 2, respectively, depicted in Fig. 6 (complexes 9 and 10). While the S–Au–P unit in 10 is practically linear (ca. 177.4°), apparent bending of the S–Au–P angle of azulene in 8 is undoubtedly a consequence of the Au···Au bonding reinforced further by the

![Fig. 1](image1.png) 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](image2.png) Fig. 2 2,6-Diisocyano-1,3-diethoxycarbonylazulene (1), 2,6-dimercapto-1,3-diethoxy-carbonylazulene (2), and their hypothetical hybrids 3a and 3b.

![Fig. 3](image3.png) Fig. 3 DFT-calculated electric dipole moments (in Debye) of azulene and its derivatives.
“aromatic donor-acceptor interactions”.37 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 for 8.29

The metric parameters for the octahedral [−(NC)Cr(CO)5] core in 8 are quite similar to those observed for 9 (ref. 32) and many other complexes [ArylNCr(CO)5].39 Comparison of the Cr–CN and C≡N bond distances49 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 −SAuPPh3 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≡CF2.44

Compounds 4–8 are highly coloured substances. The lowest energy electronic absorption band for 5 occurs at 484 nm (ε = 1.55 × 103 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).31,44 The UV-vis spectra of 6 and 7 are nearly identical and feature very intense absorption bands at 454 (ε = 3.1 × 104 M−1 cm−1) and 452 (ε = 2.6 × 104 M−1 cm−1), respectively, that have a substantial contribution from the dπ(Cr) → pπ*(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 metalation 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 PMe3 groups instead of OEt and PPh3, respectively. (Fig. 8b) but also more than doubles in intensity (ε = 5.4 × 104 M−1 cm−1). This intensity gain is due to the addition of the n(S) → pπ*(CNazulenyl) character to the HOMO → LUMO transition observed for 8 (cf. the 445 nm band for 10 in Fig. 7).29 As in the case of 9 and 10,8,29,32 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
expanded the above family of four related complexes [[OC]₅Cr(2-
isoxyano-6-X-1,3-diehoxycarbonylazulene)] [X = S(CH₂CH₂CO₂CH₂CH₃) > SCH₂CH₂CO₂CH₂CH₃ > S H >
H > Br > N≡C], the δ(C(═N)) 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-
isoxyano-6-X-azulene ligand. Concomitantly, both δ(COtrans)
and δ(COcis) 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, σpara, it is more appropriate to interpret ∆δ(CO)
and ∆δ(CN) 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 rela-
tionships δ(COtrans) vs. δ(CN) and δ(COcis) vs. δ(CN), 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)₅] 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(COtrans) vs. δ(CN) and δ(COcis) vs. δ(CN) plots that, in

Fig. 8 DFT-calculated Frontier MO’s of (a) 7 and (b) 8a, a truncated model of 8.

Table 2 ¹³C NMR data for the [Cr(CO)₅(CN)] moiety in complexes
(RNC)Cr(CO)₅

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(CN)</th>
<th>δ(COtrans)</th>
<th>δ(COcis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃P/AuS</td>
<td>178.55</td>
<td>217.26</td>
<td>214.91</td>
</tr>
<tr>
<td>CH₃IO(C₅H₄CH₂CO₂)</td>
<td>181.72</td>
<td>216.85</td>
<td>214.68</td>
</tr>
<tr>
<td>CN</td>
<td>182.27</td>
<td>216.77</td>
<td>214.65</td>
</tr>
<tr>
<td>F₃C–NCCr(CO)₅</td>
<td>183.36</td>
<td>216.69</td>
<td>214.60</td>
</tr>
<tr>
<td>F₃C=[F]C–NCCr(CO)₅</td>
<td>184.42</td>
<td>216.52</td>
<td>214.47</td>
</tr>
<tr>
<td>ClF₃C(ClF)₃–NCCr(CO)₅</td>
<td>186.6</td>
<td>216.3</td>
<td>214.4</td>
</tr>
</tbody>
</table>

Fig. 7 UV-vis spectra of 7, 8, and 10 (ref. 29) in CH₂Cl₂ at 25 °C.

Table 1 Selected bond distances and angles for 8, 9, and (RNC)
Cr(CO)₅ [R = iBu, C₂F₃]

<table>
<thead>
<tr>
<th>Bond/Distance</th>
<th>d(Cr–CN), Å</th>
<th>d(C═N), Å</th>
<th>∠(C–N–C), °</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(iBuNC)Cr(CO)₅]</td>
<td>2.016(2)</td>
<td>1.150(2)</td>
<td>177.9(2)</td>
</tr>
<tr>
<td>(iBu)Cr(CO)₅</td>
<td>1.960(6)</td>
<td>1.153(7)</td>
<td>172.6(6)</td>
</tr>
<tr>
<td>(MeCN)Cr(CO)₅</td>
<td>1.969(5)</td>
<td>1.158(6)</td>
<td>173.3(5)</td>
</tr>
<tr>
<td>(PETCN)Cr(CO)₅</td>
<td>1.953(4)</td>
<td>1.166(4)</td>
<td>167.5(3)</td>
</tr>
<tr>
<td>(F₂C₂NC)Cr(CO)₅</td>
<td>1.990(2)</td>
<td>1.162(2)</td>
<td>173.6(2)</td>
</tr>
</tbody>
</table>

a Ref. 41. b Data for two crystallographically unique molecules. c Ref. 32.

d Ref. 43.
addition to the 2-isocyanoazulenic complexes, include (OC)₅Cr(CNR) with R = C₆F₅, C₆F₃, CF₃CF₂Cl, CF₃, and CF₃ (ref. 48) are shown in Fig. 10, which again demonstrates excellent inverse-linear correlations now spanning substantially wider Δδ(13CN) and Δδ(13CO) windows.

The above δ(13CO)/δ(13CN) 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 of carbonyl 13C chemical shifts with the corresponding CO force constants (kCO) for complexes (RNC)Cr(CO)₅. Unfortunately, changes in kCO due to mild electronic perturbations of the R group are often not clearly discernible. Determining the values of kCO’s under the Cᵥ symmetry for complexes (RNC)₅Cr(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 rC=O vibrational profile (Jr=CO = 2A₁ + B₁ + E, e.g., Fig. 11 (ref. 55 and 56) and Table S17). In the IR spectra of LM(CO)₅ species, the lower energy rC=O(A₁) band is often obscured by the intense rC=O(E) band which compromises the accuracy of experimental determination of this rC=O(A₁) value (vide infra).

Similar to the trend in δ(13CN) for the (RNC)Cr(CO)₅ adducts in Table 2, the 13C 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 azulenic 6-position (δ = 179.9, 178.0, 177.5, 176.3 ppm in CDCl₃ for X = H, CH₃, OCH₃, CH₂CH₂CO₂CH₂CH₃, respectively). Yet, the rC=O stretching frequency for these free 2-isocyanoazulenes (2126 ± 1 cm⁻¹ in CH₂Cl₂) is insensitive to the nature of the group X. However, upon proceeding from 8 to (6, 7, 11) to 12 to 9, the rC=O band undergoes a small red shift (Table 3), thereby suggesting decrease in the σ-donor/π-acid ratio of the isocyanide 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 rC=H and rN=C bands at 2583 and 2140 cm⁻¹, respectively, it features a typical pattern in the rC=O stretching region for a LM(CO)₅ species. The band at 2049 cm⁻¹ corresponds to the rC=O mode A₁(1) where all five CO vibrations are nearly degenerate as Fig. 12a shows.

![Fig. 9](image-url) (a) Plot of δ(13CO)trans vs. δ(13CN) chemical shifts (in CDCl₃) in the 13C NMR spectra of 6, 7, 8, 9, 11, and 12. (b) Plot of δ(13CO)cis vs. δ(13CN) chemical shifts (in CDCl₃) in the 13C NMR spectra of 6, 7, 8, 9, 11, and 12.

![Fig. 10](image-url) (a) Plot of δ(13CO)trans vs. δ(13CN) chemical shifts (in CDCl₃) in the 13C NMR spectra of all compounds from Table 2. (b) Plot of δ(13CO)cis vs. δ(13CN) chemical shifts (in CDCl₃) in the 13C NMR spectra of all compounds from Table 2.
Table 3  IR signatures of the [(NC)Cr(CO)5] core in 6, 7, 8, 9, 11, and 12 (in CH2Cl2)

<table>
<thead>
<tr>
<th>r(CO)(A1)</th>
<th>r(CO)(A1^(2))</th>
<th>r(CO)(B1)</th>
<th>r(CO)(A1^(2) + E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>8</td>
<td>2144</td>
<td>2054</td>
<td>2003</td>
</tr>
<tr>
<td>6</td>
<td>2140</td>
<td>2050</td>
<td>2000</td>
</tr>
<tr>
<td>7</td>
<td>2140</td>
<td>2049</td>
<td>2000</td>
</tr>
<tr>
<td>11</td>
<td>2140</td>
<td>2049</td>
<td>2001</td>
</tr>
<tr>
<td>12</td>
<td>2137</td>
<td>2047</td>
<td>2002</td>
</tr>
<tr>
<td>9</td>
<td>2135</td>
<td>2043</td>
<td>2002</td>
</tr>
</tbody>
</table>

a Ref. 32.

ligands vibrate in-phase (cf. Fig. 11). The very weak band at 2000 cm⁻¹ is due to the r(C=O) vibration of B1 symmetry, which is IR-forbidden under the strict C₁ᵥ symmetry but gains slight intensity because of minor deviations of the structure from the idealized C₁ᵥ geometry. The intense r(C=O) band at 1958 cm⁻¹ chiefly represents the doubly degenerate vibration of E symmetry. This r(C=O)(E) mode obscures the remaining IR-active r(C=O) mode A1^(2). Interestingly, perturbations of the local C₁ᵥ symmetry in 7 through crystal packing interactions in the solid state are sufficient to split the E-mode into two separate r(C=O) peaks while unmasking the original A1^(2) mode (Fig. 12b).

Exposing ca. 1 × 1 cm² gold substrates to a 2 mM solution of 7 in CHCl₃ 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 H₂. The reflection absorption infrared (RAIR) spectrum of the SAM of 7 on Au(111) is shown in Fig. 13a. In addition to the r(N≡C) absorption at 2135 cm⁻¹, it features two r(C≡O) bands. The r(C≡O) region in this RAIR spectrum, however, is quite different from that in Fig. 11a in terms of peak intensities and energies. The lowest energy intense r(C≡O) band in the solution IR spectrum of 7, which is primarily attributed to the r(C≡O) mode of E symmetry, practically vanishes upon the SAM formation, while simultaneously uncovering the hidden A1^(2) band of much lower intensity. This observation implies approximately parallel orientation of the cis-CO ligands with respect to the gold surface. Indeed, surface IR selection rules dictate that only vibrations contributing to dipole changes perpendicular to the surface are IR-active. Consequently, any vibrations occurring nearly parallel to the surface would have low IR intensity. Given that the C–N–C unit in 7 is expected to be essentially linear, the appearance of the RAIR spectrum in Fig. 13a suggests upright orientation (i.e., straight C–S–Au(surface) angle) of the molecules in the SAMs of 7.

The “hollow-linear” coordination of organic thiolates in their SAMs on Au(111), akin to that depicted in Fig. 13b, has been predicted to accommodate the strongest S–Au interaction and induce S → Au(111) charge transfer via S(3p)–Au π-bonding. In the context of the chemistry presented herein, this means that the gold surface would effectively function as an electron-withdrawing “substituent,” thus, enhancing π-acidity of the 2-isocynoazulene ligand and, in turn, decreasing electron richness of the [Cr(CO)₅] unit. The A1^(1) and A1^(2) r(C≡O) bands at 2058 and 1995 cm⁻¹ in the RAIR spectrum in Fig. 11 both exhibit significant blue shifts compared to the corresponding r(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 A1^(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 r(C≡O) A1^(2) mode compared to that of the A1^(1) mode upon chemisorption of 7 stems from the greater contribution of the trans-CO stretch to the former.

The tilt angle of the aromatic moiety in SAMs of benzenoid mercaptoarenes on Au(111) can be highly variable. We have recently shown that 2-mercaptopazoene and several of its derivatives form monolayer films on Au(111) with approximately upright assembly of the azulenylthiolate constituents. Our optical ellipsometry measurements on multiple SAM samples of 7 provided consistent SAM thickness values that nicely corrobore 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. Notably, neither RAIR spectroscopic nor ellipsometric data collected for the SAMs of 7 on Au(111) would be consistent.
Cr(CO)₅ moiety served as a distinctly informative thicknesses (in Å) of the SAMs of 7, 6-mercapto-1,3-diethoxycarbonylazulene, and 6-mercapto-2-chloro-1,3-diethoxycarbonylazulene

<table>
<thead>
<tr>
<th>Mercaptoazulene derivative</th>
<th>D_{obs}</th>
<th>D_{calc}</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>

*Average of five measurements at different spots on multiple SAM samples. 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_surface angle and the Au(111)–S distance of 2.45 Å [ref. 58].

with the “on-top-bent” or any other adsorption models of 7 invoking a bent C–S–Au_surface geometry. The ellipsometric measurements on SAM films formed from our recently reported 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 π-linker terminated with both mercapto and isocyano junction moieties. Anchoring the 2-isocyano end of this linker was an important prerequisite to successfully installing its 6-mercapto terminus. The ¹³C NMR signatures of the octahedral [−(NC)Cr(CO)₅] core in related complexes 6, 7, 8, 9, 11, and 12 provided a sensitive spectroscopic handle for tuning electron richness of the Cr⁵-centre through mediation by the 2,6-azulenic framework. Moreover, the remarkably consistent inverse-linear trends δ¹³CO/δ¹³CN and δ¹³CO/δ¹¹CN for a wide spectrum of complexes (RNC)Cr(CO)₅ offer a simple and more accurate alternative to the δ¹³CO/k_CO strategy in quantifying electronic influence of the substituent R in isocyanide ligands. This ¹³C NMR approach utilizes feedback from the entire [−(NC)Cr(CO)₅] unit rather than focusing on the [Cr(CO)₅] fragment in the δ¹³CO/k_CO method. In addition, the C₅-symmetric [−(CN)Cr(CO)₅] moiety served as a distinctly informative ρ_{N=C}/ρ_{C=O} infrared reporter for probing self-assembly of the 6-mercaptoazulenic motif on the Au(111) surface. We hope that the chemistry of the 2-isocyano-6-mercaptoazulenic platform introduced herein will facilitate further development and experimental validation of the emerging concept of asymmetric anchoring relevant to the design of organic electronics materials. Efforts to access and isolate completely free (i.e., unmetalated) 3a are currently in progress.

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Notes and references


39 Average value for two crystallographically unique molecules.
41 The differences in Cr–CO
trans
C≡O
trans
average Cr–CO
cis
and average C≡O
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.
56 Cf. the experimentally observed IR-active νCO’s of 2071 (A1
(1)
) and 1964 (A1
(2)
+ E) cm
−1