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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 isocyano (-N≡C) termini 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 π-linker equipped with one mercapto and one isocyano terminus. The 2-isocyano-6-mercaptoazulene platform was efficiently accessed from 2-amino-6-bromo-1,3-diethoxycarbonylazulene in four steps. The 2-N=C end of this 2,6-azulenic motif was anchored to the [Cr(CO)\textsubscript{5}] fragment prior to formation of its 6-SH terminus. Metalation of the 6-SH end of [(OC)\textsubscript{5}Cr(-2-isocyano-1,3-diethoxycarbonyl-6-mercaptoazulene)]\textsuperscript{2-} (7) with Ph\textsubscript{3}PAuCl, under basic conditions, afforded X-ray structurally characterized heterobimetallic \textit{Cr}/Au ensemble [(OC)\textsubscript{5}Cr(μ-η\textsuperscript{2}-2-isocyano-1,3-diethoxycarbonyl-6-azulenyliithiolate)AuPh\textsubscript{3}] (8). Analysis of the \textsuperscript{13}C NMR chemical shifts for the [(N)Cr(CO)\textsubscript{3}] core in a series of the related complexes [(OC)\textsubscript{5}Cr(2-isocyano-6-X-1,3-diethoxycarbonylazulene)] (X = -N≡C, Br, H, SH, SCH\textsubscript{2}CH\textsubscript{2}CO\textsubscript{2}CH\textsubscript{3}, SAuPh\textsubscript{3}) unveiled remarkably consistent inverse-linear correlations \(δ(13C_{vnm})\) vs. \(δ(13C_{CN})\) and \(δ(13C_{vnm})\) vs. \(δ(13C_{CN})\) that appear to hold well beyond the above 2-isocyanoazulenic series to include complexes [(OC)\textsubscript{5}Cr(CN)\textsubscript{2}] containing strongly electron-withdrawing substituents R, such as CF\textsubscript{3}, CFC\textsubscript{3}, and CF\textsubscript{3}O. In addition to functioning as a sensitive \textsuperscript{13}C NMR handle, the essentially C\textsuperscript{3}-symmetric [(-NC)Cr(CO)\textsubscript{5}] moiety proved to be an informative, remote, \textit{ν}_{\text{CN}}/\textit{ν}_{\text{CO}} 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.\textsuperscript{1-3} Even though dimercapto- and diisocyno-functionalized molecular linkers have long been attracting interest of theorists\textsuperscript{4-9} and experimentalists\textsuperscript{10-15} in the quest for efficient organoelectronic materials,\textsuperscript{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,\textsuperscript{21} whereas free organic isocyanides are unlikely to tolerate chemical environments typically involved in the syntheses of mercaptans (thiols).\textsuperscript{22-24} 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.\textsuperscript{25,26} In their elegant approach to covalently bind nickel clusters to a gold surface via the 4-isocyanoenophyllithiolate bridge, Kubiak and coworkers attached both -N≡C ends of otherwise non-isolable 1,2-bis(4-isocyno-phenyl)disulfide to trinuclear nickel clusters in the \(\mu_{3}\text{η}^{3}\) fashion.\textsuperscript{25} The resulting salt, \([\{\mu_{3}(\text{η}^{3})\text{μ}_{3}(\text{μ}^{-}\text{dpmm})(\text{μ}_{3})\text{η}^{1}(\text{C=N}2\text{C}_{2}\text{H}_{2}L_{2})(\text{η}^{1}\text{L}_{3})\}^{2+}(I^{+})]\) (dpmm = bis(diphenylphosphino)methane), underwent homolysis of its S-S moiety upon exposure to a gold surface to give rectifying, presumably ionic, monolayer films.\textsuperscript{26}

Earlier this year, Ratner and Van Dyck proposed a new paradigm for the design of efficient molecular rectifiers that involved two π-conjugated units asymmetrically anchored to metallic electrodes and separated by a decoupling bridge.\textsuperscript{27} Their intriguing theoretical study suggested mercapto and cyano (-C≡N) junctions for accommodating the asymmetric anchoring on the premises that the -SH and -C≡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.\textsuperscript{27} We note that, from a practical standpoint, mercapto/isocyno...
Fig. 1 (a) Polar resonance form of azulene and C-atom numbering scheme of the azulenic scaffold; (b) Frontier molecular orbitals of azulene.

asymmetric anchoring would be worth considering as well, given that the isocyno group offers a substantially more stable junction within a wider range of organometallic platforms compared to its isomeric cyan congener. 

Herein, we introduce chemistry of the first, to the best of our knowledge, π-conjugated 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 physicochemical characteristics, complementary orbital density distributions within its Frontier molecular orbitals (Fig. 1). 

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-isocyano-6-mercaptop-1,3-diethoxycarbonylazulene (3a) and 2-mercaptop-6-isocyano-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 “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-formamidino-6-bromo-1,3-diethoxycarbonylazulene 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), 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 Cr0 adduct 6. No product featuring the thioether S:Cr(CO)5 interaction35 was documented in this reaction. The [(-NC)Cr(CO)5] moiety of 6 tolerated the basic environment and subsequent acidification of the reaction mixture used to convert 6 into auburn organometallic thiol 7, which constitutes 3a with its 2-NC terminus anchored to the 16-e [Cr(CO)5] fragment. Metalation of the 6-SH end of 7 with PPh3AuCl under basic conditions yielded orange-red crystals of heterobimetallic Cr0/AuI complex 8 after a simple workup.

The solid-state structure of 8·1/2CH2Cl2 features two very similar but crystallographically independent molecules of 8 in
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characterized mononuclear Cr
Au1-S1 165.82(5), Au1-S1-C1 108.1(2), C12-N1-C17 172.6(6), Cr1-C17-N1 175.3(5).

O8 1.155(8), C19-O7 1.141(6), C20-O6 1.142(6), C21- O9 1.146(7), C22-O5 1.147(7), P1-
2.268(1), Au1-S1 2.318(1), S1-C1 1.744(5), Cr1-C17 1.960(6), Cr1-C18 1.901(8), Cr1-C19
and C
perturbations do not significantly affect the Au-S- C angle in

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Table 1 Selected bond distances and angles for 8, 9, and (RNC)Cr(CO), [R = \text{Bu}, C,F,].

|            | \(d(\text{Cr-CN})\) Å | \(d(\text{C=N})\) Å | \(\angle(\text{C-N-C})\) ° |
|------------|----------------------|---------------------|--------------------------|
| \(\text{BuNC})\Cr(CO)\ | 2.016(2)             | 1.150(2)            | 177.9(2)                 |
| 8          | 1.960(6), 1.969(5) 1.155(7), 1.158(6) 172.6(6), 173.3(5) |
| 9          | 1.953(4)            | 1.166(4)            | 167.5(3)                 |
| \(\text{F,C,F})\Cr(CO)\ | 1.909(2)             | 1.162(2)            | 173.6(2)                 |

\*Ref. 41; \*data for two crystallographically unique molecules; \*ref. 32; \*ref. 43.

Compounds 4 – 8 are highly coloured substances. The lowest energy electronic absorption band for 5 occurs at 484 nm (\(\epsilon = 1.55 \times 10^3\) 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),\(^{31,44}\) The UV-Vis spectra of 6 and 7 are nearly identical and feature very intense absorption bands at 454 (\(\epsilon = 3.1 \times 10^4\) M\(^{-1}\) cm\(^{-1}\)) and 452 (\(\epsilon = 2.6 \times 10^4\) M\(^{-1}\) cm\(^{-1}\)), respectively, that have a substantial contribution from the \(\text{d(\gamma,\gamma′)}\rightarrow\text{\pi^*(CNAzulenyl)}\) charge transfer (Figs. 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, Ref. 32; 8b) but also more than doubles in intensity (\(\epsilon = 5.4 \times 10^4\) M\(^{-1}\) cm\(^{-1}\)). This intensity gain is due to the addition of the n(S)→\pi^*(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,\(^{29,32}\) the LUMOs of 7 and 8a constitute the \(\pi^*\)-system of the azulenic moiety with contributions from both anchoring groups while their HOMOs involve the entire 2-isocyano-6-azulenylthiolate motif (Fig. 8).

![Fig. 5 Molecular structure of one of the two crystallographically independent molecules of 8 (50% thermal ellipsoids).](Image 72x604 to 289x723)

![Fig. 6 Previously X-ray structurally characterized mononuclear Cr\(^{II}\) and Au complexes 9\(^{19,30}\) and 10\(^{35}\).](Image 316x112 to 538x293)

the asymmetric unit that are linked together via a weak
Au⋯Au interaction\(^{36}\) of 3.2102(4) Å (Figs. 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 Phring of the other molecule’s PPh\(_3\) 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\(^{II}\) and Au\(^{III}\) adducts of 1 and 2, respectively, depicted in Fig. 6 (complexes 9\(^{12}\) and 10\(^{35}\)). 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 “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° 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 ([L-NC]Cr(CO)\(_3\) core in 8 are quite similar to those observed for 9\(^{35}\) and many other complexes (aryl[NC]Cr(CO))\(_3\).\(^{39}\) Comparison of the Cr-CN and C=N bond distances\(^{35}\) for 8 and 9 (Table 1) may hint that the 2-isocyanooazulene ligand in 8 has a somewhat higher \(\alpha\)-donor/\(\pi\)-acceptor ratio than that in 9, thereby reflecting the difference in electron-donating/withdrawing characteristics of –SAuPP\(_3\) 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 \(d(\text{Cr-CN})\) and \(d(\text{C=N})\) are

![Fig. 7 UV-Vis spectra of 7, 8, and 10\(^{37}\) in CH\(_2\)Cl\(_2\) at 25 °C.](Image 316x112 to 538x293)
Whilst considering $^{13}$C NMR signatures of the [(NC)Cr(CO)$_2$] 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)$_2$Cr(2-isocyano-6-X-1,3-diethoxycarbonylazulene)] ($X = $F, Cl, Br, $\equiv$C) to include species with $\sigma$-donor/$\pi$-acceptor ratio of the Cr-centre's electron richness mediated by the paramagnetic shielding term, $\sigma_{\text{para}}$, which reflects the degree of $\pi$-backbonding.

Fig. 9(a) shows a truncated model of complexes, include (OC)$_2$Cr(CO)$_2$ of Table 2 unveiled remarkably consistent inverse-linear relationships $\Delta \delta^{(13)\text{CO}}$ vs. $\delta^{(13)\text{CN}}$ and $\delta^{(13)\text{CO}}$ 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 $^{13}$C chemical shifts of terminal CO and CNR ligands in low-valent complexes are influenced considerably by the paramagnetic shielding term, $\sigma_{\text{para}}$, it is more appropriate to interpret $\Delta \delta^{(13)\text{CN}}$ and $\Delta \delta^{(13)\text{CO}}$ as a combined $\sigma$-donor/$\pi$-acceptor effect.

Closer examination of the $^{13}$C NMR data in the top six rows of Table 2 unveiled remarkably consistent inverse-linear relationships $\Delta \delta^{(13)\text{CO}_{\text{trans}}}$ vs. $\delta^{(13)\text{CN}}$ and $\delta^{(13)\text{CO}_{\text{cis}}}$ vs. $\delta^{(13)\text{CN}}$, as illustrated in Fig. 9. This figure also confirms that remote modulation of 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)$_2$] moiety. Would the trends depicted in Fig. 9 hold beyond the 2-isocyanoazulenic series? To address this question, we considered (RNC)Cr(CO)$_2$ species containing strongly electron-withdrawing substituents R, for which $^{13}$C NMR data acquired in the same solvent (CDCl$_3$) were available (bottom four rows in Table 2). The expanded $\delta^{(13)\text{CO}_{\text{trans}}}$ vs. $\delta^{(13)\text{CN}}$ and $\delta^{(13)\text{CO}_{\text{cis}}}$ vs. $\delta^{(13)\text{CN}}$ plots that, in addition to the 2-isocyanoazulenic complexes, include (OC)$_2$Cr(CNR) with R = C$_6$F$_5$, C$_6$F$_3$, CFCIF$_2$C$_6$F$_4$, and C$_6$F$_4$ are shown in Fig. 10, which again demonstrates excellent inverse-linear correlations now spanning substantially wider $\Delta \delta^{(13)\text{CN}}$ and $\Delta \delta^{(13)\text{CO}}$ windows.

\[\begin{array}{|c|c|c|c|}
\hline
\text{Compound} & \delta^{(13)\text{CN}} & \delta^{(13)\text{CO}_{\text{trans}}} & \delta^{(13)\text{CO}_{\text{cis}}} \\
\hline
(\text{a}) & 193.8 & 214.6 & 213.3 \\
(\text{b}) & 199.3 & 214.2 & 213.0 \\
(\text{c}) & 208.2 & 212.0 & 212.0 \\
(\text{d}) & 211.1 & 211.5 & 211.7 \\
\hline
\end{array}\]

All spectra were recorded in CDCl$_3$.
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Fig. 10 (a) Plot of $\delta^{13\text{CN}}$ vs. $\delta^{13\text{CO}}$ chemical shifts (in CDCl$_3$) in the $^{13}\text{C}$ NMR spectra of all compounds from Table 2; (b) plot of $\delta^{13\text{CO}}$ vs. $\delta^{13\text{CN}}$ chemical shifts (in CDCl$_3$) in the $^{13}\text{C}$ NMR spectra of all compounds from Table 2.

The above $\delta^{\text{13CO}}/\delta^{\text{13CN}}$ 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 the carbonyl $^{13}\text{C}$ chemical shifts with the corresponding CO force constants ($k_{\text{CO}}$) for complexes (RNC)Cr(CO)$_3$. Unfortunately, changes in $k_{\text{CO}}$ due to mild electronic perturbations of the R group are often not clearly discernible. Determining the values of $k_{\text{CO}}$’s under the $C_{\text{av}}$ symmetry for complexes (RNC)Cr(CO)$_3$ 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 $\nu_{\text{CO}}$ vibrational profile (e.g., Fig. 11 and Table S17). In the IR spectra of LM(CO)$_3$ species, the lower energy $\nu_{\text{CO}}(A_2)$ band is often obscured by the intense $\nu_{\text{CO}}(E)$ band, which compromises the accuracy of experimental determination of this $\nu_{\text{CO}}(A_2)$ value (vide infra).

Fig. 11 DFT-calculated $\nu_{\text{CO}}$ vibrational profile for (MeNC)Cr(CO)$_3$ in the gas phase.

Table 3 IR signatures of the [(NC)Cr(CO)$_3$] core in 6, 7, 8, 9, 11, and 12 in CH$_2$Cl$_2$.

| $\nu_{\text{CO}}(A_1)$ cm$^{-1}$ | $\nu_{\text{CO}}(A_{1}^{(2)})$ cm$^{-1}$ | $\nu_{\text{CO}}(B_1)$ cm$^{-1}$ | $\nu_{\text{CO}}(A_{1}^{(2)})+\nu_{\text{E}}$ cm$^{-1}$ |
|-----------------------------|-----------------|-----------------|-------------------------------|
| 6                          | 2144            | 2054            | 2003                          | 1957                          |
| 7                          | 2140            | 2050            | 2000                          | 1958                          |
| 11                         | 2140            | 2049            | 2001                          | 1959                          |
| 12                         | 2137            | 2047            | 2002                          | 1960                          |
| 9                          | 2135            | 2043            | 2002                          | 1962                          |

Similar to the trend in $\delta^{13\text{CN}}$ for the (RNC)Cr(CO)$_3$ adducts in Table 2, the $^{13}\text{C}$ NMR resonance for the terminal C-atom in the available uncoordinated 2-isocyanoazulenes moves upfield upon increasing electron-donating power of the substituent X at the azulenic 6-position ($\delta = 179.9^{56}$, 178.0, 177.5, 176.3 ppm in CDCl$_3$ for X = N,C, Br, H, SCH$_2$CH$_2$CH$_2$CH$_2$H, respectively). Yet, the $\nu_{\text{NC}}$ stretching frequency for these free 2-isocynoazulenes (2126±1 cm$^{-1}$ in CH$_2$Cl$_2$) is insensitive to the nature of the group X. However, upon proceeding from 6 to (7, 8, 11) to 12 to 9, the $\nu_{\text{NC}}$ band undergoes a small red shift (Table 3), thereby suggesting decreasing in the $\alpha$-donor/$\pi$-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 CH$_2$Cl$_2$. In addition to the characteristic $\nu_{\text{SH}}$ and $\nu_{\text{NC}}$ bands at 2583 and 2140 cm$^{-1}$, respectively, it features a typical pattern in the $\nu_{\text{CO}}$ stretching region for a LM(CO)$_3$ species. The band at 2049 cm$^{-1}$ corresponds to the $\nu_{\text{CO}}(A_1)$ where all five CO ligands vibrate in-phase (cf. Fig. 11). The very weak band at 2000 cm$^{-1}$ is due to the $\nu_{\text{CO}}(E)$ vibration of $B_1$-symmetry, which is IR-forbidden under the strict $C_{\text{av}}$ symmetry but gains slight intensity because of minor deviations of the structure from the idealized $C_{\text{av}}$ geometry. The intense $\nu_{\text{CO}}(E)$ band at 1958 cm$^{-1}$ chieflly represents the doubly degenerate vibration of E-symmetry. This $\nu_{\text{CO}}(E)$ band obscures the remaining IR-active $\nu_{\text{CO}}$ mode $A_1^{(2)}$. Interestingly, perturbations of the local $C_{\text{av}}$ symmetry in 7 through crystal packing interactions in the solid state are sufficient to split the E-mode into two separate $\nu_{\text{CO}}$ peaks while unmasking the original $A_1^{(2)}$ mode (Fig. 12b).

Fig. 12 FTIR spectra of 7 in (a) CH$_2$Cl$_2$ and (b) KBr.
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 Figure 13a. In addition to the ν₅ carbonyl absorption at 2135 cm⁻¹, it features two ν₃ bands. The ν₃ 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 ν₃ band in the solution IR spectrum of 7, which is primarily attributed to the ν₃ 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-carbonyl 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 thiols 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-isocyanocarbazole ligand and, in turn, decreasing electron richness of the [Cr(CO)₅]₄⁻ unit. The A₁(1) and A₁(2) ν₃ bands at 2058 and 1995 cm⁻¹ in the RAIR spectrum in Fig. 11 both exhibit significant blue shifts compared to the corresponding ν₃ bands 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(1) mode, to be attributed solely to differences in intermolecular interactions within the SAM vs. solution of 7. The larger change in energy of the ν₃ bands 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-mercaptoazulene and several of its derivatives form monolayer films on Au(111) with approximately upright assembly of the azulenyliothiole constitutents. 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.

Notably, neither RAIR spectroscopic nor ellipsometric data collected for the SAMs of 7 on Au(111) would be consistent 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-mercaptop-1,3-diethoxybenzylazene and 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene also corroborate that these 6-mercaptopaluenoles 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-isocyanide end of this linker was an important prerequisite to successfully installing its 6-mercaptop terminus. The ¹³C NMR signatures of the octahedral [(-NC)Cr(CO)₅]₄⁻ core in related complexes 6, 7, 8, 9, 11, and 12 provided a sensitive spectroscopic handle for tuning electron richness of the Crᴵ centre through mediation by the 2,6-azulenyl framework. Moreover, the remarkably consistent inverse-linear trends δ¹³(COᴰ₁)⁻¹³(COₓ) and δ¹³(COₓ⁻¹³(COₓ) for a wide spectrum of complexes (RNCr(CO)₅) offer a simple and more accurate alternative to the δ¹³(CO)/k₁₀ 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 δ¹³(CO)/k₁₀ method. In addition, the Cₛ-symmetric [(-CN)Cr(CO)₅] moiety served as a distinctly informative ν₃/Cₐᵥ infrared reporter for probing self-assembly of the 6-mercaptopaluenolic motif on the Au(111).

Table 4 Observed ellipsometric (D_ref) and calculated (D_fit) film thicknesses (in Å) of the SAMs of 7, 6-mercaptop-1,3-diethoxybenzylazulene, and 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene

| Mercaptoazulene derivative | D_refᵃ | D_fitᵇ |
|---------------------------|--------|--------|
| 7                         | 18.3±2.7 | 17.1 |
| 6-mercaptop-1,3-diethoxybenzylazulene | 12.8±1.9 | 13.3 |
| 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene | 14.6±1.9 | 13.3 |

ᵃ Average of five measurements at different spots on multiple SAM samples; calculated from the X-ray structural data for 8, 6-mercaptop-1,3-diethoxybenzylazulene (ref. 29), and 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene (ref. 29), as well as by assuming straight C-S-Au_surface angle and the Au(111)-S distance of 2.45 Å (ref. 57).

Table 4 Observed ellipsometric (D_ref) and calculated (D_fit) film thicknesses (in Å) of the SAMs of 7, 6-mercaptop-1,3-diethoxybenzylazulene, and 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene

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| 6-mercaptop-1,3-diethoxybenzylazulene | 12.8±1.9 | 13.3 |
| 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene | 14.6±1.9 | 13.3 |

ᵃ Average of five measurements at different spots on multiple SAM samples; calculated from the X-ray structural data for 8, 6-mercaptop-1,3-diethoxybenzylazulene (ref. 29), and 6-mercaptop-2-chloro-1,3-diethoxybenzylazulene (ref. 29), as well as by assuming straight C-S-Au_surface angle and the Au(111)-S distance of 2.45 Å (ref. 57).
surface. We hope that the chemistry of the 2-isocynano-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

1 Functional Supramolecular Architectures: For Organic Electronics and Nanotechnology, ed. P. Samori and F. Cacilai, Wiley-VCH, Weinheim, 2011, vol. 1-2.
2 M. V. Barybin, J. J. Meyers, Jr. and B. M. Neal in Isocyanide Chemistry - Applications in Synthesis and Material Science Nenajdenko, V., Ed. Wiley-VCH: Weinheim, 2012, pp 493-529.
3 M. Lasar and R. J. Angelici in Modern Surface Organometallic Chemistry; J.-M Basset, R. Psaro, D. Roberto and R. Ugo, Eds.; Wiley-VCH: Weinheim, 2009; pp 513-556.
4 M. Bürkle, J. K. Viljas, D. Vonlanthen, A. Mishchenko, G. Schönn, M. Mayor, T. Wandlowski and F. Pauly, Phys. Rev. B, 2012, 85, 075417.
5 H. Häkkinen, Nature Chem., 2012, 4, 443.
6 C. Morari, G.-M. Rignanese and S. Melinte, Phys. Rev. B, 2007, 76, 115428.
7 Y. Li, D. Lu, S. A. Swanson, J. C. Scott and G. Galli, J. Phys. Chem. C., 2008, 112, 6413.
8 C. Chu, J. A. Ayres, D. M. Stefanescu, B. R. Walker, C. B. Gorman and G. N. Parsons, J. Chem. Phys. C, 2007, 111, 8080.
9 R. B. Pontes, A. R. Rocha, S. Sanvito, A. Fazzio and A. J. R. da Silva, ACS Nano, 2011, 5, 795.
10 J. Kestell, R. Abuflah, M. Garvey and W. T. Tysoe, J. Phys. Chem. C, 2015, 119, 23042.
11 C. Bruot, J. Hihath and N. Tao, Nat. Nanotechnol., 2012, 7, 35.
12 Y. Kim, T. Pietsch, A. Erbe, W. Belzig and E. Scheer, Nano Lett., 2011, 11, 3734.
13 B. Kim, S. H. Choi, X. Y. Zhu and C. D. Frisbie, J. Am. Chem. Soc., 2011, 133, 19864.
14 B. Kim, J. M. Beebe, Y. Jun, X.-Y. Zhu and C. D. Frisbie, J. Am. Chem. Soc., 2006, 128, 4970.
15 K. L. Murphy, W. T. Tysoe and D. W. Bennett, Langmuir, 2004, 20, 1732.
16 C. A. Mirkin and Mark A. Ratner, Annu. Rev. Phys. Chem., 1992, 43, 719.
17 J. C. Love, L. A. Estoff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, Chem. Rev., 2005, 105, 1103.
18 B. K. Pathem, S. A. Claridge, Y. B. Zheng and P. S. Weis, Annu. Rev. Phys. Chem., 2013, 64, 605.
19 D. K. James and I. M. Tour, Chem. Mater., 2004, 16, 4423.
20 S. H. Choi, B. Kim and C. D. Frisbie, Science, 2008, 320, 1482.
21 I. Ugi, Isotitride Chemistry, Academic Press: New York, 1971.
22 R. J. Cremlyn, An Introduction to Organosulfur Chemistry, John Wiley & Sons LTD: 1996.
23 C. M. Rayner, Contemp. Org. Synth., 1996, 3, 499.
24 I. V. Koval’, Russ. J. Org. Chem., 2005, 41, 631.
25 G. M. Ferrence, J. I. Henderson, D. G. Kurth, D. A. Morgenstern, T. Bein and C. P. Kubiak, Langmuir, 1996, 12, 3075.
26 J. I. Henderson, S. Feng, G. M. Ferrence, T. Bein and C. P. Kubiak, Inorg. Chem. Acta, 1996, 242, 115.
27 C. Van Dyck and M. A. Ratner, Nano Lett., 2015, 15, 1577.
28 S. Vosskötter, P. Konieczny, C. M. Marian and R. Weinkauf, Phys. Chem. Chem. Phys., 2015, 17, 23573.
29 K. J. Scheetz, A. D. Spaeth, A. S. Vorushilov, D. R. Powell, V. W. Day and Mikhail V. Barybin, Chem. Sci., 2013, 4, 4267.
30 M. Koch, O. Blacque, K. Venkatesan, J. Mater. Chem. C, 2013, 1, 7400.
31 T. R. Maher, A. D. Spaeth, B. M. Neal, C. L. Berrie, W. H. Thompson, V. W. Day and M. V. Barybin, J. Am. Chem. Soc., 2010, 132, 15924.
32 T. C. Holovics, R. E. Robinson, E. C. Weinrobat, M. Toriyama, G. H. Lushington and M. V. Barybin, J. Am. Chem. Soc., 2006, 128, 2300.
33 M. V. Barybin, M. H. Chisholm, N. S. Dalal, T. H. Holovics, N. J. Patmore, R. E. Robinson and D. J. Zipse, J. Am. Chem. Soc., 2005, 127, 15182.
34 This compound is accessible in three high-yielding steps from commercially available 2-chlorotropon and ethyl cyanooacetate: T. Nozoe, S. Seto, S. Matsumura and Y. Murase, Bull. Chem. Soc. Jpn., 1962, 35, 1179.
35 H. G. Raubenheimer, M. W. Estersuyhsen, G. Frenking, A. Y. Timoshkin, C. Estersuyhsen and U. E. I. Horvath, Dalton Trans., 2006, 4580.
36 H. Schmidbaur and A. Schier, Chem. Soc. Rev., 2012, 41, 370.
37 C. R. Martinez and B. L. Iverson, Chem. Sci., 2012, 3, 2191.
38 C. Janiak, J. Chem. Soc., Dalton Trans., 2000, 3885.
39 Average value for two crystallographically unique molecules.
40 A. E. Carpenter, C. C. Mokhtarzadeh, S. Di. Ripatti, I. Havrylyuk, R. Kamezawa, C. E. Moore, A. L. Rheingold and J. S. Figueroa, Inorg. Chem., 2015, 54, 2936.
41 The differences in Cr-CO\textsubscript{trans}, Cr-CO\textsubscript{cis}, average Cr-CO\textsubscript{avg}, and average CrO\textsubscript{avg} bond lengths in 8 and 9 are insignificant.
42 W. Sattler and G. Parkin, Chem. Commun., 2009, 7566 and CCDC # 744953.
43 D. Lentz and D. Preugschat, Chem. Commun., 1992, 1523.
44 An EWG at position 2 of the azulenic framework stabilizes the LUMO without significantly affecting the HOMO: S. V. Shevyakov, H. Li, R. Muthyala, A. E. Asato, J. C. Croney, D. M. Jameson and R. S. H. Liu, J. Phys. Chem. A, 2003, 107, 3295.
45 M. V. Barybin, W. W. Brennessel, B. E. Kucera, M. E. Minyaev, V. J. Sussman, V. G. Young, Jr. and J. E. Ellis, J. Am. Chem. Soc., 2007, 129, 1141.
46 L. J. Todd and J. R. Wilkinson, J. Organomet. Chem., 1974, 77, 1.
47 D. Lentz, M. Anibarro, D. Preugschat and G. Bertrand, J. Fluorine Chem., 1998, 89, 73.
48 D. Lentz, Chem. Ber., 1984, 117, 415.
49 O. A. Gyansow, B. Y. Kimura, G. R. Dobson and R. A. Brown, J. Am. Chem. Soc., 1971, 93, 5922.
50 D. L. Cronin, J. R. Wilkinson and L. J. Todd, J. Magn. Reson., 1975, 17, 353.
51 R. J. Dennenberg and D. J. Daresbourg, Inorg. Chem., 1972, 11, 72.
52 F. A. Cotton and C. S. Krahnzeln, J. Am. Chem. Soc., 1962, 84, 4432.
53 R. B. King and M. S. Saran, Inorg. Chem., 1972, 13, 74.
54 D. Karakas and C. Kaya, J. Organomet. Chem., 2001, 640, 37.
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 $\nu_{\mathrm{CO}}$'s of 2071 (A1$^{(1)}$) and 1964 (A1$^{(2)}$+E) cm$^{-1}$ for (MeNC)Cr(CO)$_5$ in n-hexanes: J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1972, 1247.

57 M. Y. Darensbourg, *Prog. Inorg. Chem.*, 1985, 33, 221.

58 A. Cossaro, R. Mazzarello, R. Rousseau, L. Casalis, A. Verdini, A. Kohlmeyer, L. Floreano, S. Scandolo, A. Morgante, M. L. Klein and G. Scoles, *Science*, 2008, 321, 943-946.

59 H. A. Pearce and N. Sheppard, *Surface Sci.*, 1976, 59, 205.

60 M. Tachibana, K. Yoshizawa, A. Ogawa, H. Fujimoto and Roald Hoffmann, *J. Phys. Chem. B*, 2002, 106, 12727.

61 H. Sellers, A. Ultman, Y. Shnidman and J. E. Eilers, *NATO ASI Series B: Physics*, 1992, 283, 441.

62 M. S. Davies, R. S. Armstrong and M. J. Aroney, *Chimika Chronika, New Series*, 1995, 24, 233.

63 B. M. Neal, A. S. Vorushilov, A. M. DeLaRosa, R. E. Robinson, C. L. Berrie and M. V. Barybin, *Chem. Commun.*, 2011, 47, 10803.

64 D. L. Dubose, R. E. Robinson, T. C. Holovics, D. R. Moody, E. C. Weintrob, C. L. Berrie and M. V. Barybin, *Langmuir*, 2006, 22, 4599-4606.