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## Supplementary Information for

Ancillary nitrile substituents as convenient IR  
spectroscopic reporters for self-assembly of  
mercapto- and isocyanoazulenes on Au(111)

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## 1. Syntheses and characterization of compounds 1 -5

**General procedures and starting materials.** Synthetic operations that require inert atmosphere conditions were performed under an atmosphere of 99.5% argon purified by passage through columns of activated BASF catalyst and molecular sieves. Standard Schlenk techniques were employed with a double manifold vacuum line. Solvents, including deuterated solvents, were freed of impurities by standard procedures and stored under argon.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with samples sealed in 0.1 mm NaCl cells or between NaCl disks. NMR samples were analyzed on Bruker Avance 400 or 500 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are given with reference to residual solvent resonances relative to  $\text{SiMe}_4$ . Elemental analyses were carried out by Chemisar Laboratories Inc. (Ontario, Canada) and Columbia Analytical Services (Tucson, Arizona). 2-Chloro-1,3-diethoxycarbonylazulene,<sup>1</sup> 2-amino-1,3-dicyanoazulene,<sup>2</sup> 1,3-dicyanoazulene,<sup>3</sup> and acetic-formic anhydride<sup>4</sup> were synthesized according to published procedures. All other reagents were obtained from commercial sources. Davisil (200-425 mesh, type 60A) silica gel was used for chromatographic purifications.

**Synthesis of 2-mercapto-1,3-diethoxycarbonylazulene (1).** Red crystals of 2-Chloro-1,3-diethoxycarbonylazulene (0.320 g, 1.04 mmol) and 3.00 g of 68% aqueous sodium hydrosulfide (36.4 mmol) were added to 30 mL of 70% aqueous ethanol. The resulting solution/slurry was brought to reflux and stirred for 2 hrs. After cooling to room temperature, the mixture was stirred for an additional 10 hrs. Then the flask contents were diluted with 100 mL of water and extracted with pentane (2×100 mL). Acidification of the aqueous layer with sulfuric acid afforded an orange precipitate, which was extracted with  $\text{CH}_2\text{Cl}_2$  (2×100 mL). The combined methylene chloride extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under vacuum and the residue was passed through a short (*ca.* 10 cm length × 5 cm OD) silica gel column using neat  $\text{CHCl}_3$ . After solvent removal and drying at  $10^{-2}$  torr, brick-red crystalline **1** (0.208 g, 0.683 mmol) was isolated in a 66% yield. Anal. calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}$ : C, 63.14; H, 5.30. Found: C, 63.32; H, 4.93. FTIR ( $\text{CHCl}_3$ ):  $\nu_{\text{SH}}$  2480 w br,  $\nu_{\text{CO}}$  1683 s, 1660 m sh  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  1.50 (t,  $^3J_{\text{HH}} = 8$  Hz, 6H,  $\text{CH}_3$ ), 4.49 (q,  $^3J_{\text{HH}} = 8$  Hz, 4H,  $\text{CH}_2$ ), 7.58 (t,  $^3J_{\text{HH}} = 10$  Hz and 12 Hz, 2H,  $\text{H}^{5,7}$ ), 7.69 (t,  $^3J_{\text{HH}} = 12$  Hz, 1H,  $\text{H}^6$ ), 7.71 (s, 1H, SH) 9.34 (dd,  $^3J_{\text{HH}} = 10$  Hz and 12 Hz, 2H,  $\text{H}^{4,8}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  14.5 ( $\text{CH}_3$ ), 60.7 ( $\text{CH}_2$ ), 113.7, 131.7, 135.5, 138.0, 143.9, 155.7, 166.0 ( $\text{CO}_2\text{Et}$ ) ppm.

The original synthesis of **1** from 2-chloro-1,3-diethoxycarbonylazulene in an 89% yield employed methyl 3-mercaptopropionate in a two-step procedure.<sup>5</sup> The  $^1\text{NMR}$  data for **1** reported in ref. 5 are very similar to those described herein.

**Synthesis of 2-mercaptoazulene (2).** Compound **1** (0.150 g, 0.493 mmol) was heated in *ca.* 25 mL of 100%  $\text{H}_3\text{PO}_4$  at 115 °C for 1 hr and then at 130° for an additional 1 hr.<sup>6</sup> After cooling to room temperature, the reaction mixture was diluted with 200 mL of water and extracted with benzene (2×30 mL). The combined organic extracts were dried over anhydrous sodium sulfate. The drying agent was filtered off and the concentrated filtrate was subject to column chromatography on silica gel (*ca.* 20 cm length × 3 cm OD) using benzene as eluent. A bluish-purple band was collected, from which 0.060 g (0.374 mmol) of **2** was isolated in a 76% yield as purple crystals. Anal. calcd. for  $\text{C}_{10}\text{H}_8\text{S}$ : C, 74.96; H, 5.03. Found: C, 74.40; H, 4.43. FTIR

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(CHCl<sub>3</sub>):  $\nu_{\text{SH}}$  2579 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  3.88 (s, 1H, SH), 7.12 (s, 2H, H<sup>1,3</sup>), 7.14 (dd, <sup>3</sup>J<sub>HH</sub> = 12 Hz and 10 Hz, 2H, H<sup>5,7</sup>), 7.44 (t, J = 10 Hz, 1H, H<sup>6</sup>), 8.04 (d, <sup>3</sup>J = 12 Hz, 2H, H<sup>4,8</sup>) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  116.6, 124.5, 133.0, 135.4, 140.7, 140.8 ppm.

Compound **2** can also be synthesized from 2-hydroxy-1,3-diethoxycarbonylazulene and dimethylthiocarbamyl chloride in three steps in a 41% yield.<sup>7</sup> The <sup>1</sup>NMR data for **2** reported in ref. 7 are essentially identical to those described herein.

**Synthesis of 2-chloro-1,3-dicyanoazulene (3).** A solution/slurry of 1,3-cyano-2-aminoazulene (0.200 g, 1.04 mmol) in 250 mL of toluene was saturated with dry hydrogen chloride. To this mixture, 0.15 mL of isoamyl nitrite (1.1 mmol) was added and the resulting reaction mixture was stirred for 48 hrs at room temperature. Then, the mixture was filtered and the filter-cake was washed with CH<sub>2</sub>Cl<sub>2</sub> until the washings were colorless. The organic fractions were combined, washed with water, brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated on a rotary evaporator and the oily residue was subject to column chromatography on silica gel (*ca.* 25 cm length × 3 cm OD) using neat CH<sub>2</sub>Cl<sub>2</sub> as eluent. The first eluted band provided 0.081 g (0.381 mmol) of red microcrystalline **3** in a 37% yield after solvent removal. Mp: 316 – 318 °C (lit. “over 300 °C”<sup>7</sup>). IR (THF):  $\nu_{\text{CN}}$  2223 m cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.94 (t, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, H<sup>5,7</sup>), 8.16 (t, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 1H, H<sup>6</sup>), 8.74 (d, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, H<sup>4,8</sup>) ppm. <sup>13</sup>C NMR (126 MHz, DMF-d<sub>7</sub>, 25 °C):  $\delta$  97.5, 113.9, 134.7, 139.7, 143.4, 144.0, 145.0 ppm.

In our opinion, the above procedure is significantly more convenient compared to the original synthesis of **3** from 2-hydroxy-1,3-dicyanoazulene and POCl<sub>3</sub> in a sealed tube at 150 °C that required distillation of excess POCl<sub>3</sub>.<sup>8</sup>

**Synthesis of 2-mercapto-1,3-dicyanoazulene (4).** To a solution/slurry of **3** (0.100 g, 0.470 mmol) in 100 mL of ethanol, 6.0 g of 68% aqueous sodium hydrosulfide (73 mmol) diluted with 20 mL of water was added and the reaction mixture was refluxed for 45 min. After cooling to room temperature, the mixture was diluted with 300 mL of H<sub>2</sub>O and extracted Et<sub>2</sub>O (2×100 mL). The aqueous fraction was acidified with concentrated sulfuric acid to form a pink precipitate. The mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×100 mL) and the combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The drying agent was filtered off. The solvent was removed from the filtrate under vacuum to afford 0.076 g (0.257 mmol) of pink **4**·CH<sub>2</sub>Cl<sub>2</sub> (55%). Anal. calcd. for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>S: C, 52.89; H, 2.73; N, 9.49. Found: C, 53.07; H, 2.68; N, 9.26. FTIR (Nujol mull):  $\nu_{\text{CN}}$  2208 s,  $\nu_{\text{SH}}$  2554 w cm<sup>-1</sup>. FTIR (THF):  $\nu_{\text{CN}}$  2215 s cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  4.78 (br s, 1H, SH), 5.32 (CH<sub>2</sub>Cl<sub>2</sub> solvate), 7.82 (t, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 2H, H<sup>5,7</sup>), 7.99 (t, <sup>3</sup>J<sub>HH</sub> = 10 Hz, 1H, H<sup>6</sup>), 8.52 (d, <sup>3</sup>J<sub>HH</sub> = 10 Hz 2H, H<sup>4,8</sup>) ppm. <sup>13</sup>C NMR (126.0 MHz, C<sub>5</sub>D<sub>5</sub>N, 25 °C):  $\delta$  104.14, 119.8, 125.3, 130.6, 131.5, 148.6 ppm.

**Synthesis of 2-isocyano-1,3-dicyanoazulene (5).** An orange slurry of 2-amino-1,3-dicyanoazulene (1.02g, 5.28 mmol) in 50mL of neat acetic-formic anhydride was stirred for 15 hrs with gentle heating. The reaction mixture was then brought to room temperature and a pink flamingo solid was filtered off, washed extensively with CH<sub>2</sub>Cl<sub>2</sub>, and dried under vacuum to afford the crude product (1.058 g, 4.78 mmol), presumably 2-formamido-1,3-dicyanoazulene. Without further purification, a portion of this product (0.2337g, 1.056 mmol) was combined with triethylamine (0.5 mL, 3.6 mmol) and phosphorous oxychloride (0.14 mL, 1.5 mmol) in 25 mL

of anhydrous  $\text{CH}_2\text{Cl}_2$  under argon atmosphere. The resulting solution/slurry was stirred for 15 min at room temperature and then quenched with 100 mL of 10%  $\text{KHCO}_3$ . The organic layer was separated and the aqueous layer was washed with 30 mL of  $\text{CH}_2\text{Cl}_2$ . The combined organic fractions were washed with water ( $4 \times 30$  mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The drying agent was filtered off. The filtrate was concentrated under vacuum and subjected to chromatography on a short silica gel column (*ca.* 10 cm length  $\times$  5 cm OD) using neat  $\text{CH}_2\text{Cl}_2$  to elute a purple band. All solvent was removed under vacuum and the residue was dried at  $10^{-2}$  torr to afford **5** (0.1215g, 0.5985 mmol) as somewhat air-sensitive, raspberry-coloured microcrystals in a 52% yield based on 2-amino-1,3-dicyanoazulene). HRMS (*m/z*, ES<sup>-</sup>, 2 nM solution in  $\text{CH}_3\text{CN}/\text{NH}_4\text{OAc}$ ): found for  $[\text{M}-\text{H}]^-$  202.0401; calcd for  $\text{C}_{13}\text{H}_4\text{N}_3$  202.0405. MS (*m/z*, ES<sup>+</sup>): 203.1 ( $[\text{M}^+]$ ). FTIR ( $\text{CHCl}_3$ ):  $\nu_{\text{CN}}$  2224 vs, 2114  $\text{s cm}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.05 (t,  $^3J_{\text{HH}} = 10$  Hz, 2H,  $H^{5,7}$ ), 8.31 (t,  $^3J_{\text{HH}} = 10$  Hz, 1H,  $H^6$ ), 8.87 (d,  $^3J_{\text{HH}} = 10$  Hz 2H,  $H^{4,8}$ ) ppm.  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  95.8, 112.1, 133.2, 141.1, 142.1, 144.8, 180.5 (*isocyano* -NC) ppm.

## 2. X-ray structure determination for **1**

X-ray quality crystals of **1** were grown by layering pentane over a nearly saturated solution of this compound in  $\text{CH}_2\text{Cl}_2$  at room temperature and then cooling the sample to +4 °C for several days. All manipulations with the crystals prior to transfer to the goniometer were performed in air. A full hemisphere of diffracted intensities (1850 10-second frames with a  $\omega$  scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System.<sup>9</sup> X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 2984 reflections. A total of 8429 integrated reflection intensities having  $2\theta(\text{MoK}\alpha) < 61.04^\circ$  were produced using the Bruker program SAINT.<sup>10</sup> The data were corrected empirically for variable absorption effects using equivalent reflections. The Bruker software package SHELXTL was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using  $F_o^2$  data with the SHELXTL Version 6.10 software package.<sup>11</sup>

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All hydrogen atoms were located in a difference Fourier and included in the structural model as independent isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles. The thiol group was included in the final cycles of least-squares refinement as a rigid rotor (assuming idealized  $\text{sp}^3$ -hybridized geometry and a S-H bond length of 1.20 Å) that was allowed to rotate about its S-C bond; the isotropic thermal parameter of the thiol hydrogen was refined. A total of 251 parameters were refined using no restraints, 4139 data and weights of  $w = 1/[\sigma^2(F^2) + (0.0788 P)^2]$ , where  $P = [F_o^2 + 2F_c^2]/3$ . Crystal data, data collection, solution, and refinement information for **1** are summarized in Table S1. Tables S2 through S7 contain atomic coordinates, as well as metric and displacement parameters for **1**.

**Table S1.** Crystal data and structure refinement for **1**.

Empirical formula	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub> S	
Formula weight	304.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$ – C <sub>i</sub> <sup>1</sup> (No. 2)	
Unit cell dimensions	a = 6.782(1) Å	α = 100.453(3)°
	b = 9.952(1) Å	β = 94.859(3)°
	c = 11.066(2) Å	γ = 103.049(3)°
Volume	709.3(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.425 Mg/m <sup>3</sup>	
Absorption coefficient	0.241 mm <sup>-1</sup>	
F(000)	320	
Crystal size	0.40 x 0.15 x 0.11 mm <sup>3</sup>	
Theta range for data collection	2.55° to 30.52°	
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15	
Reflections collected	8429	
Independent reflections	4139 [R <sub>int</sub> = 0.050]	
Completeness to theta = 30.52°	95.5 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.632	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4139 / 0 / 251	
Goodness-of-fit on F <sup>2</sup>	1.059	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.056, wR <sub>2</sub> = 0.136	
R indices (all data)	R <sub>1</sub> = 0.067, wR <sub>2</sub> = 0.143	
Largest diff. peak and hole	0.68 and -0.48 e <sup>-</sup> /Å <sup>-3</sup>	

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**. U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
S(1)	3433(1)	2955(1)	2779(1)	22(1)
O(1)	1979(2)	-1590(1)	829(1)	21(1)
O(2)	3299(2)	2368(1)	6833(1)	21(1)
O(3)	2719(2)	705(1)	760(1)	29(1)
O(4)	3481(2)	3877(1)	5552(1)	25(1)
C(1)	2498(2)	75(2)	2713(2)	17(1)
C(2)	2913(2)	1464(2)	3424(2)	17(1)
C(3)	2901(2)	1419(2)	4697(2)	17(1)
C(4)	2339(3)	-538(2)	5891(2)	19(1)
C(5)	2035(3)	-1914(2)	6069(2)	20(1)
C(6)	1783(3)	-3163(2)	5213(2)	21(1)
C(7)	1693(3)	-3351(2)	3934(2)	21(1)
C(8)	1873(3)	-2344(2)	3198(2)	19(1)
C(9)	2501(2)	-22(2)	4800(2)	16(1)
C(10)	2251(2)	-878(2)	3536(2)	16(1)
C(11)	2421(3)	-210(2)	1364(2)	19(1)
C(12)	1874(3)	-1907(2)	-514(2)	23(1)
C(13)	1273(3)	-3492(2)	-906(2)	26(1)
C(14)	3252(3)	2672(2)	5699(2)	18(1)
C(15)	3657(3)	3558(2)	7867(2)	24(1)
C(16)	3390(3)	2952(2)	9008(2)	26(1)

**Table S3.** Bond lengths [Å] for **1**.

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S(1)-C(2)	1.739(2)	C(6)-C(7)	1.387(3)
S(1)-H(1S)	1.20	C(6)-H(6)	0.92(2)
O(1)-C(11)	1.348(2)	C(7)-C(8)	1.393(2)
O(1)-C(12)	1.454(2)	C(7)-H(7)	0.98(2)
O(2)-C(14)	1.343(2)	C(8)-C(10)	1.397(2)
O(2)-C(15)	1.450(2)	C(8)-H(8)	0.90(2)
O(3)-C(11)	1.215(2)	C(9)-C(10)	1.473(2)
O(4)-C(14)	1.216(2)	C(12)-C(13)	1.508(3)
C(1)-C(2)	1.415(2)	C(12)-H(12A)	0.97(2)
C(1)-C(10)	1.423(2)	C(12)-H(12B)	0.94(2)
C(1)-C(11)	1.463(2)	C(13)-H(13A)	0.97(3)
C(2)-C(3)	1.418(2)	C(13)-H(13B)	0.95(2)
C(3)-C(9)	1.426(2)	C(13)-H(13C)	1.02(3)
C(3)-C(14)	1.470(2)	C(15)-C(16)	1.503(3)
C(4)-C(5)	1.391(2)	C(15)-H(15A)	0.94(2)
C(4)-C(9)	1.398(2)	C(15)-H(15B)	1.02(2)
C(4)-H(4)	0.96(2)	C(16)-H(16A)	0.95(2)
C(5)-C(6)	1.386(2)	C(16)-H(16B)	0.98(3)
C(5)-H(5)	0.94(2)	C(16)-H(16C)	0.93(3)

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**Table S4.** Bond angles [°] for **1**.

C(2)-S(1)-H(1S)	109.5	C(1)-C(10)-C(9)	107.0(1)
C(11)-O(1)-C(12)	115.5(1)	O(3)-C(11)-O(1)	122.0(2)
C(14)-O(2)-C(15)	116.1(1)	O(3)-C(11)-C(1)	123.8(2)
C(2)-C(1)-C(10)	108.3(1)	O(1)-C(11)-C(1)	114.3(1)
C(2)-C(1)-C(11)	121.9(1)	O(1)-C(12)-C(13)	106.2(2)
C(10)-C(1)-C(11)	129.8(2)	O(1)-C(12)-H(12A)	107(1)
C(1)-C(2)-C(3)	109.5(1)	C(13)-C(12)-H(12A)	109(1)
C(1)-C(2)-S(1)	123.1(1)	O(1)-C(12)-H(12B)	110(1)
C(3)-C(2)-S(1)	127.4(1)	C(13)-C(12)-H(12B)	110(1)
C(2)-C(3)-C(9)	107.9(1)	H(12A)-C(12)-H(12B)	114(2)
C(2)-C(3)-C(14)	124.2(1)	C(12)-C(13)-H(13A)	110(2)
C(9)-C(3)-C(14)	127.9(2)	C(12)-C(13)-H(13B)	109(2)
C(5)-C(4)-C(9)	129.9(2)	H(13A)-C(13)-H(13B)	108(2)
C(5)-C(4)-H(4)	113(1)	C(12)-C(13)-H(13C)	108(1)
C(9)-C(4)-H(4)	117(1)	H(13A)-C(13)-H(13C)	111(2)
C(6)-C(5)-C(4)	129.8(2)	H(13B)-C(13)-H(13C)	111(2)
C(6)-C(5)-H(5)	120(1)	O(4)-C(14)-O(2)	121.7(2)
C(4)-C(5)-H(5)	110(1)	O(4)-C(14)-C(3)	125.1(2)
C(5)-C(6)-C(7)	128.0(2)	O(2)-C(14)-C(3)	113.2(1)
C(5)-C(6)-H(6)	116(1)	O(2)-C(15)-C(16)	106.3(1)
C(7)-C(6)-H(6)	116(1)	O(2)-C(15)-H(15A)	105(1)
C(6)-C(7)-C(8)	129.0(2)	C(16)-C(15)-H(15A)	112(1)
C(6)-C(7)-H(7)	117(1)	O(2)-C(15)-H(15B)	109(1)
C(8)-C(7)-H(7)	114(1)	C(16)-C(15)-H(15B)	110(1)
C(7)-C(8)-C(10)	130.0(2)	H(15A)-C(15)-H(15B)	114(2)
C(7)-C(8)-H(8)	116(1)	C(15)-C(16)-H(16A)	114(1)
C(10)-C(8)-H(8)	114(1)	C(15)-C(16)-H(16B)	111(1)
C(4)-C(9)-C(3)	126.7(2)	H(16A)-C(16)-H(16B)	109(2)
C(4)-C(9)-C(10)	126.0(2)	C(15)-C(16)-H(16C)	111(2)
C(3)-C(9)-C(10)	107.3(1)	H(16A)-C(16)-H(16C)	105(2)
C(8)-C(10)-C(1)	125.9(2)	H(16B)-C(16)-H(16C)	106(2)
C(8)-C(10)-C(9)	127.1(2)		

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**Table S5.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
S(1)	32(1)	9(1)	24(1)	7(1)	1(1)	5(1)
O(1)	33(1)	12(1)	19(1)	3(1)	3(1)	6(1)
O(2)	34(1)	11(1)	20(1)	2(1)	4(1)	8(1)
O(3)	50(1)	14(1)	24(1)	7(1)	5(1)	6(1)
O(4)	39(1)	10(1)	28(1)	5(1)	5(1)	7(1)
C(1)	20(1)	9(1)	22(1)	4(1)	2(1)	4(1)
C(2)	18(1)	10(1)	24(1)	6(1)	2(1)	4(1)
C(3)	20(1)	9(1)	22(1)	4(1)	2(1)	4(1)
C(4)	21(1)	13(1)	22(1)	5(1)	3(1)	5(1)
C(5)	25(1)	14(1)	21(1)	7(1)	3(1)	4(1)
C(6)	25(1)	11(1)	29(1)	9(1)	2(1)	4(1)
C(7)	26(1)	9(1)	27(1)	4(1)	1(1)	3(1)
C(8)	23(1)	11(1)	22(1)	3(1)	1(1)	3(1)
C(9)	16(1)	10(1)	23(1)	5(1)	2(1)	4(1)
C(10)	17(1)	11(1)	21(1)	4(1)	2(1)	4(1)
C(11)	23(1)	12(1)	23(1)	5(1)	2(1)	5(1)
C(12)	34(1)	16(1)	19(1)	4(1)	3(1)	7(1)
C(13)	38(1)	16(1)	23(1)	2(1)	2(1)	9(1)
C(14)	21(1)	11(1)	23(1)	4(1)	3(1)	6(1)
C(15)	36(1)	12(1)	23(1)	0(1)	4(1)	7(1)
C(16)	31(1)	22(1)	23(1)	4(1)	4(1)	6(1)

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**Table S6.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**.

	x	y	z	U(eq)
H(1S)	3943	3990	3592	78(10)
H(4)	2620(30)	140(20)	6660(20)	27(6)
H(5)	2070(30)	-1920(20)	6920(20)	23(5)
H(6)	1640(30)	-3960(20)	5530(20)	29(6)
H(7)	1350(30)	-4320(20)	3470(20)	27(6)
H(8)	1730(30)	-2680(20)	2379(19)	20(5)
H(12A)	3230(30)	-1560(20)	-712(18)	23(5)
H(12B)	880(30)	-1530(20)	-869(19)	22(5)
H(13A)	1210(40)	-3760(30)	-1800(20)	41(7)
H(13B)	-40(40)	-3830(30)	-690(20)	38(7)
H(13C)	2330(40)	-3880(30)	-470(20)	42(7)
H(15A)	5010(30)	4060(20)	7869(18)	20(5)
H(15B)	2600(30)	4120(20)	7740(20)	26(5)
H(16A)	2060(30)	2370(20)	8994(18)	24(5)
H(16B)	3720(40)	3690(30)	9760(20)	39(7)
H(16C)	4270(40)	2370(30)	9100(20)	44(7)

**Table S7.** Hydrogen bonds for **1** ([ $\text{\AA}$ ] and  $^\circ$ ).

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
S(1)-H(1S)...O(4)	1.20	2.24	3.034(1)	121.0
S(1)-H(1S)...O(4)#1	1.20	2.40	3.462(1)	145.9

Symmetry transformations used to generate equivalent atoms: #1:  $-x+1, -y+1, -z+1$ .

### 3. Surface studies

**Self-assembled monolayer films of 1, 2, and 5 on the Au(111) surface.** Commercial gold-coated silicon substrates (Platypus Technologies) were soaked sequentially in distilled  $\text{CHCl}_3$ , acetone, and 200-proof ethanol for one to two hours in each solvent. After drying with a stream of  $\text{N}_2$  gas, ellipsometric physical constants of the bare gold samples were taken. SAM films of **1**, **2**, or **5** were formed by immersing a freshly cleaned gold substrate into a 2 mM solution of the corresponding compound in  $\text{CHCl}_3$  for *ca.* 24 hrs. Prior to analysis, the gold sample was removed from the solution, rinsed thoroughly with anhydrous  $\text{CHCl}_3$  and dried in a flow of  $\text{N}_2$  gas. No precautions to exclude air or ambient laboratory lighting were taken during this procedure.

**Self-assembled monolayer films of 4 on the Au(111) surface.** Au(111) film samples (*ca.* 1 cm  $\times$  1 cm) prepared from commercial silicon wafers with  $\sim 1000 \text{ \AA}$  of gold coated over a titanium adhesion layer (Platypus Technologies, product code AU.1000.SL1) were soaked sequentially in distilled  $\text{CHCl}_3$ , acetone, and 200-proof ethanol for one to two hours in each solvent. After drying with a stream of  $\text{N}_2$  gas, ellipsometric physical constants of the bare gold samples were taken. SAM films of **4** were formed by immersing a freshly cleaned gold substrate into a 2 mM solution of **4** in distilled anhydrous THF for *ca.* 24 hrs. Prior to analysis, the gold sample was removed from the solution, rinsed thoroughly with anhydrous  $\text{CHCl}_3$  and ethanol and dried in a flow of  $\text{N}_2$  gas. No precautions to exclude air or ambient laboratory lighting were taken during this procedure.

**Optical ellipsometry.** The film thicknesses were determined using an Auto EL III ellipsometer (Rudolph Research). All measurements were made with a HeNe laser at a wavelength of 632.8 nm and an incident angle of  $70^\circ$  to the surface normal. The optical constants for the gold films were determined independently for each sample from the measurement on the freshly cleaned bare gold substrates. These optical constants were used in the determination of the thickness of the adsorbed organic layer. A refractive index of 1.45 was assumed<sup>12</sup> for the organic thin film described herein. At least five different spots on each SAM sample were used to take ellipsometric measurements. The reported thickness values constitute an average of the measurements over each of those spots along with the standard deviation of the measurement given in parentheses.

**Surface IR measurements.** The grazing incidence Reflection Absorption Fourier Transform Infrared Spectroscopy data for the SAMs of **1**, **2**, and **5** on gold were obtained on a nitrogen-purged Thermo Nicolet 670 FTIR spectrometer with a VeeMax grazing angle accessory set at an angle of  $70^\circ$ . Before acquiring the spectrum of the sample, a background spectrum was collected using a freshly cleaned bare gold substrate. One thousand scans from 600 to  $4000 \text{ cm}^{-1}$  at  $4 \text{ cm}^{-1}$  resolution were collected for each background/sample pair.

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**Figure S1.** RAIR spectra of a SAM sample of **4** before (A) and after (B) exposure to a solution of **5**.

