

Electronic Supplementary Information

**Homoleptic gold(I) *N*-heterocyclic allenylidene complexes:
Excited-state properties and lyotropic chromonics**

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Electronic Supplementary Information (ESI) available: Experiment details, additional spectra and tables.

Experimental Section

Materials. All starting materials were purchased from commercial sources and used as received. The solvents used for synthesis were of analytical grade unless stated otherwise. The solvents used for nanostructure preparations and photophysical measurements were of HPLC grade. The compounds THT-Au-Cl (THT = tetrahydrothiophene)^[1], L1,^[2] L2-L4,^[3] were prepared according to modified literature methods.

Characterization. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. ¹H, ¹³C and ¹⁹F NMR spectra were recorded with Bruker Avance 400 FT-NMR or 600 FT-NMR spectrometers. Elemental analyses were performed by Beijing Institute of Chemistry, Chinese Academy of Sciences. Infrared spectra were recorded on a Bio-Rad FT-IR spectrometer.

UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer. Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). Luminescent quantum yields were referenced to degassed 9,10-bis(phenylethynyl)anthracene in degassed CH₂Cl₂ (BPEA, $\Phi = 0.39$) with estimated error of $\pm 15\%$.

Time-resolved emission and transient absorption experiments were performed on an LP-920 Laser flash photolysis setup (Edinburgh Instruments). The 266/355 nm pump laser pulse was obtained from the fourth/third harmonic output of an Nd:YAG Q-switched laser, and the probe light was provided by a 450 W xenon lamp. The sample was excited by the pump laser, and the

[1] W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.*, 2004, **126**, 7639.

[2] K. H. Wong, K. K. Cheung, M. C. W. Chan, C.-M. Che, *Organometallics*, 1998, **7**, 3505.

[3] A. K. Al-sa'ady, C. A. McAuliffe, R. V. Parish, J. A. Aandbank, *Inorg. Synth.*, 1985, **23**, 191.

probe light from the xenon lamp was passed through the sample at right angles to the path of the exciting pulse. The two beams were focused onto a 1 cm quartz cell. After passing through the sample the analyzing light was directed to a monochromator/spectrograph. The transmitted probe light was then measured either by a single detector (for kinetic analysis at a single wavelength) or by an array detector (for spectral analysis at a given time). The transmission properties of the sample before, during, and after the exciting pulse were converted by the detector into electrical signals, which were measured by an oscilloscope (in the case of the single detector) or acquired by a CCD camera (in the case of an array detector). The changes in the transmission properties were converted into changes of optical density. The signals analyzed by a symmetrical Czerny-Turner monochromator were detected by a Hamamatsu R928 photomultiplier, and the signal processed via an interfaced PC and analytical software.

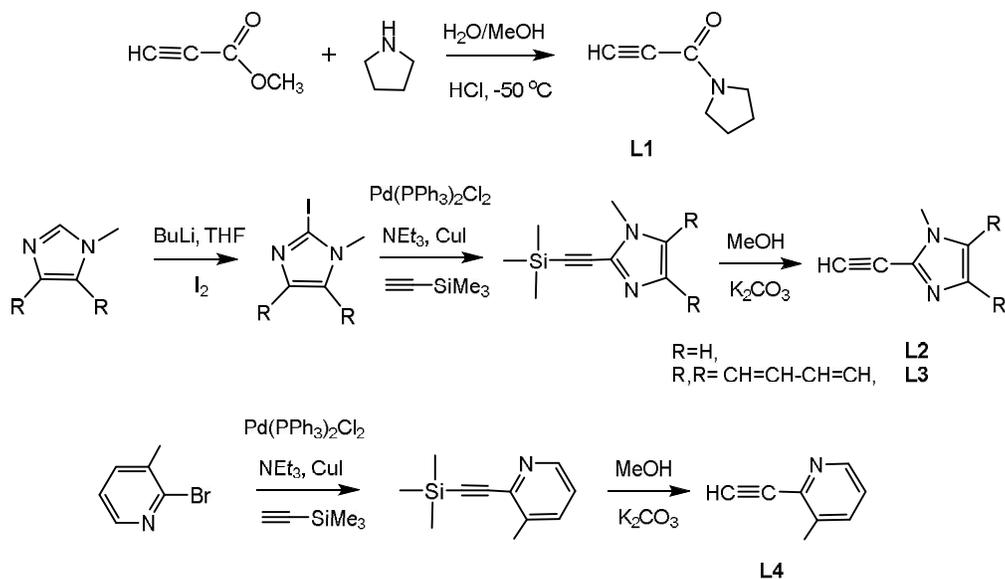
The SEM images were taken on a Hitachi S-4800 field emission scanning electron microscope operating at 3.0 kV. SEM samples were prepared by drop-casting suspensions onto silicon wafers.

Single crystals of **5**·PF₆ and **7**·PF₆ suitable for X-ray diffraction analysis were obtained by slow evaporation of the acetone/*n*-hexane solutions, while that of **8**·PF₆ was obtained by diffusion of acetonitrile/diethyl ether solutions. The diffraction data were collected by a Bruker X8 PROTEUM single crystal X-ray diffractometer with MicroStar rotating-anode X-ray source (CuK_α radiation, $\lambda = 1.54178 \text{ \AA}$). Step-scanned PXRD data was collected by Bruker AXS D8 ADVANCE (Philips PW1830) powder X-ray diffractometer, in Bragg-Brentano ($\theta/2\theta$) reflection mode with a graphite monochromatized CuK_α radiation ($\lambda = 1.540562 \text{ \AA}$) and nickel filter.

Mesophase formation and characterization. Complex **5**.Cl was dispersed in water and the suspension was heated to 65 °C in a water bath to give homogenous solutions. These samples

were cooled down to room temperature and then characterizations of the mesophase were performed. ^2H NMR spectra were recorded with a Bruker Avance 500 FT-NMR spectrometer. Mesophase textures were recorded on a polarization optical microscope (Axio Scope.A1).

Synthesis and Characterization Data



Synthetic Procedure for L1: 40 mmol pyrrolidine was dissolved in a 10 % solution of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1/1, w/w), namely 12.8 mL H_2O and 16 mL MeOH , the mixture was cooled to -50°C . Then 40 mmol methyl propiolate was added to the solution in small portion, and the mixture was stirred at -50°C for 3 hours. After that, 200 mL 2N HCl solution was added, which was further stirred at room temperature for 16 hours. Then the clear orange solution was extracted 3 times by CHCl_3 , and then washed with saturated NaHCO_3 solution and H_2O . Dried over MgSO_4 and removal of the solvent gave pure product as off-white solid.

L1. White solid; Yield: 90 %; ^1H -NMR (CDCl_3 , 400 MHz): δ 3.78 (t, 2H, $J = 4.39$ Hz), 3.65 (t, 2H, $J = 4.53$ Hz), 3.16 (s, 1H), 1.96 (m, 4H); ^{13}C -NMR (CDCl_3 , 150 MHz): δ 149.31, 78.98, 78.71, 47.53, 44.68, 24.68, 23.98; IR (KBr) 2099.8 cm^{-1} ($\text{C}\equiv\text{C}$); MS(ESI): 123.1 $[\text{M}]^+$; Elemental Analysis: C 68.27, H 7.37, N 11.37, Found: C 68.01, H 7.35, N 11.34.

Synthetic Procedures for **L2-L3**: Firstly, To a solution of 1-methylimidazole/ 1-methylbenzylimidazole (36.5 mmol) in 60 mL dry THF, 20 mL n-BuLi 2.5 M in hexane) was added dropwise over half an hour at -80 °C. After that, the mixture was stirred at room temperature for 16 hours. The mixture was washed with a Na₂S₂O₃ solution, then the organic layer was extracted by CHCl₃ and further washed with brine, dried over anhydrous Na₂SO₄. After evaporation, washing the residue with little amount of ether gave pure off-white 2-iodo-1-methylimidazole (71 %) and 2-iodo-1-methylbenzylimidazole (60 %). Secondly, 2-iodo-1-methylimidazole / 2-iodo-1-methylbenzylimidazole (2.4 mmol) was dissolved in 20 mL triethylamine, and the mixture was degassed by N₂ for 10 minutes. Pd(PPh₃)₂Cl₂ (0.1 mmol) and CuI (0,048 mmol) were added quickly, followed by the addition of 5 mmol trimethylsilyl (0.5 mL) acetylene through syringe. The mixture was firstly stirred at room temperature for 1 hour, then at 70 °C for 5 hours. The volume of solvent was reduced under low pressure at 25 °C (as the product 1-methy-2-trimethylsilylethynylimidazole is volatile). The organic layer was extracted with CHCl₃, then washed with saturated NH₄Cl solution, brine and water. Dried over anhydrous MgSO₄ and concentrated under reduced pressure, the resulting brown residue was purified by column chromatography (n-Hexane/Ethyl acetate = 3/1 to 1/1). The resulted 1-methy-2-trimethylsilylethynylimidazole was colorless oil when firstly prepared, but turned into yellow later (58 %). The 1-methy-2-trimethylsilylethynyl benzyllimidazole is off-white solid (54 %). Thirdly, 5 mmol 1-methy-2-trimethylsilylethynylimidazole/1-methy-2-trimethylsilylethynyl benzyllimidazole and 6 mmol K₂CO₃ was dissolved in 3 mL MeOH, and the mixture was stirred at room temperature for 15 minutes. The solid was filtered and the filtrate was concentrated under low pressure at room temperature to give pure **L2** as light yellow oil (93 %), and **L3** as white solid (95 %).

L2. Light yellow oil. ¹H-NMR (CDCl₃, 400 MHz): δ 7.27 (d, 1H, J = 1.07 Hz), 6.95 (d, 1H, J = 1.04 Hz), 3.74 (s, 3H), 3.32 (s, 1H); ¹³C-NMR (CDCl₃, 150 MHz): δ 139.20, 128.46, 122.32, 76.32, 75.30, 30.87; IR(KBr) 2134.5 cm⁻¹ (C≡C); MS(FAB): 106.01 [M]⁺; Elemental Analysis: C 67.90 , H 5.70, N 26.40, Found: C 67.64, H 5.71, N 26.31.

L3. White solid. ¹H-NMR (CDCl₃, 400 MHz): δ 7.70 (d, 1H, J = 7.72 Hz), 7.33 (d, 1H, J = 4.50 Hz), 7.20 (m, 2H), 3.88 (s, 3H), 3.27 (s, 1H); ¹³C-NMR (CDCl₃, 150 MHz): δ 142.75, 137.29, 134.66, 123.97, 122.92, 120.36, 109.46, 102.26, 93.41, 30.66; IR(KBr) 2167.7 cm⁻¹ (C≡C);

MS(FAB): 156.1 [M]⁺; Elemental Analysis: C 76.90 , H 5.16, N 17.94, Found: C 77.11, H 5.20, N 17.89.

Synthetic Procedures for **L4**: **L4** was synthesized by a two-step coupling starting from 2-bromo-3-methylpyridine. The synthetic details were similar to those of **L2-L3**, except that **L4** is far more stable in ambient conditions.

General Procedure for the Syntheses of Complexes 1-4·Na: A mixture of tHt-Au-Cl (3 mmol) and **L1-L4** (7 mmol) in 5 mL CH₂Cl₂ was treated with NaOCH₃ (8 mmol) in 15 mL CH₃OH. The white solution was degassed for 5 minutes by N₂ and then stirred at room temperature for overnight. After removing the solvent, the white solid was washed with ether, small portion of water followed by methanol for 2 times.

[Au(C≡CCH₃Im)₂]⁻Na⁺ (**1·Na**). Grey-white solid; Yield: 59 %; ¹H-NMR (CD₃OD, 400 MHz): δ 6.78 (d, 1H, J < 1 Hz), 6.94 (d, 1H, J < 1 Hz), 3.77 (s, 3H); ¹³C-NMR (CD₃OH, 150 MHz): δ 140.2, 136.2, 127.6, 121.3, 91.5, 33.8; IR (KBr): 2117.5 cm⁻¹ (C≡C); MS(ESI): 407.5 [M]⁺; Elemental Analysis: C 35.39 , H 2.48, N 13.76, Found: C 34.88, H 2.47, N 13.56.

[Au(C≡CCH₃benzylIm)₂]⁻Na⁺ (**2·Na**). White solid; Yield: 62 %; ¹H-NMR (CD₃OD, 400 MHz): δ 7.58 (d, 1H, J = 4.73 Hz), 7.41 (d, 1H, J = 4.48 Hz), 7.27 (t, 1H, J = 7.64), 6.59 (t, 1H, J = 8.40), 3.89 (s, 3H); ¹³C-NMR (CD₃OH, 150 MHz): δ 144.2, 142.4, 139.7, 134.4, 123.0, 122.7, 118.3, 109.6, 91.5, 30.1; IR(KBr): 2129.9 cm⁻¹ (C≡C); MS(ESI): 507.5 (M⁺); Elemental Analysis: C 41.35, H 2.78, N 11.4, Found: C 40.48, H 2.74, N 10.88.

{Au[C≡C(C=O)N(CH₂)₄]₂]⁻Na⁺ (**3·Na**). Grey-white solid; Yield: 65%; ¹H-NMR (CD₃OD, 400 MHz): δ 3.69 (t, 2H, J = 6.72 Hz), 3.57 (t, 2H, J = 6.68 Hz), 1.91 (m, 4H); ¹³C-NMR (CD₃OH, 150 MHz): δ 146.0, 139.8, 95.1, 48.8, 44.9, 25.0, 24.6; IR (KBr) 2094.4 cm⁻¹ (C≡C); MS(ESI): 441.1[M]⁺; Elemental Analysis: C 36.22 , H 3.47, N 6.03, Found: C 36.18, H 3.47, N 6.02.

{Au[C≡CPyridyl]₂]⁻Na⁺ (**4·Na**). Grey-white solid; Yield: 62%; ¹H-NMR (DMSO-*d*₆ 400 MHz): δ 8.21 (d, 1H, J = 5.46 Hz), 7.49 (d, 1H, J = 6.32 Hz), 7.05 (t, 1H, J = 6.25 Hz), 2.27 (s, 3H); ¹³C-NMR (CD₃OH, 150 MHz): δ 146.4, 145.7, 142.3, 136.0, 134.2, 120.1, 101.2, 19.6; IR (KBr) 2108.0,

2092.4 cm^{-1} ($\text{C}\equiv\text{C}$); MS(ESI): 429.1 $[\text{M}]^+$; Elemental Analysis: C 42.49, H 2.67, N 6.19, Found: C 41.86, H 2.62, N 6.13.

General Procedure for the Syntheses of Complexes 5-8·X: The acetylide complexes **1-4·Na** (1 mmol) in 20 mL dry CH_2Cl_2 were cooled down to $-50\text{ }^\circ\text{C}$, then methyl triflate (3 mmol) was added quickly through syringe. The solution was stirred at $-50\text{ }^\circ\text{C}$ for 30 minutes, then at room temperature for another 4 hours. The solvent was removed by rotatory evaporation and the excess MeOTf was washed away by ether. The complexes with triflate as anion were dissolved in methanol, which was filtered into a saturated methanolic solution of NH_4PF_6 . The resulted white precipitate was washed carefully with little amount of methanol to obtain pure **5-8·PF₆** in high yields.

5·Cl-6·Cl. **5·PF₆-6·PF₆** (1 mmol) was stirred with excess chloride exchange resin in 5 mL methanol for 15 minutes. Then the resin was removed by filtration and the resulting filtrate was dried by rotator evaporation.

5·PF₆. White solid; Yield: 88 %; $^1\text{H-NMR}$ (CD_3CN , 400 MHz): δ 7.17 (d, 2H, $J < 1$ Hz), 3.84 (s, 6H); $^{13}\text{C-NMR}$ (CD_3CN , 150 MHz): δ 158.8, 132.5, 122.4, 82.5, 36.2; $^{19}\text{F-NMR}$ (CD_3CN , 400 MHz): δ -71.2, -72.9; IR(KBr) 2113.0 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS(ESI): 437.1 $[\text{M}]^+$; Elemental Analysis: C 28.88 , H 2.77, N 9.62, Found: C 29.09, H 2.79, N 9.56.

5·Cl. White solid; Yield: 82 %; $^1\text{H-NMR}$ (CD_3OD , 400 MHz): δ 7.40 (d, 2H, $J < 1$ Hz), 3.76 (s, 6H); $^{13}\text{C-NMR}$ (CD_3OD , 150 MHz): 160.9, 132.5, 122.8, 82.5, 36.1; IR (KBr) 2113.4 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS(ESI): 437.1 $[\text{M}]^+$; Elemental Analysis: C 35.57 , H 3.41, N 11.85, Found: C 34.88, H 3.37, N 11.68.

6·PF₆. White solid; Yield: 88 %; $^1\text{H-NMR}$ (CD_3CN , 400 MHz): δ 7.72 (d, 2H, $J = 3.25$ Hz), 7.65 (t, 2H, $J = 3.05$), 3.94 (s, 6H); $^{13}\text{C-NMR}$ (CD_3CN , 150 MHz): δ 164.5, 136.2, 132.2, 127.7, 113.4, 82.3, 33.3; $^{19}\text{F-NMR}$ (CD_3CN , 400 MHz): δ -72.0, -73.4; IR (KBr) 2109.6 cm^{-1} ($\text{C}=\text{C}=\text{C}$); MS(ESI): 537.1 $[\text{M}]^+$; Elemental Analysis: C 38.72, H 2.95, N 8.21, Found: C 38.52, H 2.93, N 8.19.

6·Cl. White solid; Yield: 88 %; $^1\text{H-NMR}$ ($\text{DMSO-}d_6$ 400 MHz): δ 7.68 (d, 2H, $J = 3.39$ Hz), 7.53 (t, 2H, $J = 3.18$), 3.90 (s, 6H); $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$ 150 MHz): δ 165.2, 133.9, 131.5, 126.6, 113.3,

83.1, 32.6; IR(KBr) 2109.1 cm^{-1} (C=C=C); MS(ESI): 537.1 $[\text{M}]^+$; Elemental Analysis: C 46.13, H 3.52, N 9.78, Found: C 45.59, H 3.54, N 9.69.

7·PF₆. White solid; Yield: 82 %; ¹H-NMR (CD₃CN, 400 MHz): δ 4.21 (s, 3H), 3.85 (t, 2H, J = 5.48 Hz), 3.60 (t, 2H, J = 5.74 Hz), 1.94 (m, 4H); ¹³C-NMR (CD₃CN, 150 MHz): δ 166.2, 132.0, 86.3, 61.0, 52.4, 46.8, 24.1, 23.7; ¹⁹F-NMR (CD₃CN, 400 MHz): δ -71.8, -73.7; IR(KBr) 2113.8 cm^{-1} (C=C=C); MS(ESI): 471.2 $[\text{M}]^+$; Elemental Analysis: C 31.18, H 3.60, N 4.55, Found: C 31.08, H 3.58, N 4.57.

8·PF₆. Grey-white solid; Yield: 86 %; ¹H-NMR (CD₃CN, 400 MHz): δ 8.30 (d, 1H, J = 5.84 Hz), 8.15 (d, 1H, J = 6.53 Hz), 7.52 (t, 1H, J = 6.77 Hz), 4.45 (s, 3H), 2.53 (s, 3H); ¹³C-NMR (CD₃CN, 150 MHz): δ 167.9, 144.4, 143.5, 142.4, 123.4, 119.0, 94.4, 48.3, 20.5; ¹⁹F-NMR (CD₃CN, 400 MHz): δ -72.0, -73.9; IR(KBr) 2111.5, 2083.4 cm^{-1} (C=C=C); MS(ESI): 459.1 $[\text{M}]^+$; Elemental Analysis: C 35.78, H 3.00, N 4.64, Found: C 36.56, H 2.96, N 4.61.

Table S1. Crystal Data

	5 ·PF ₆	7 ·PF ₆	8 ·PF ₆
formula	C ₄₂ H ₄₈ N ₁₂ F ₁₈ P ₃ Au ₃	C ₁₈ H ₁₈ F ₆ N ₂ O ₂ PAu	C ₂₀ H ₂₁ F ₆ N ₃ PAu
fw	1786.69	636.28	645.33
color	colorless	colorless	light yellow
crystal size	0.15 × 0.04 × 0.03	0.05 × 0.05 × 0.02	
crystal system	triclinic	orthorhombic	orthorhombic
space group	<i>P</i> -1	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pnma</i>
<i>a</i> , Å	11.7938(2)	7.32120(10)	15.7075(7)
<i>b</i> , Å	13.6822(2)	13.6716(2)	6.8525(3)
<i>c</i> , Å	13.8013(7)	21.2142(14)	20.3447(10)
<i>α</i> , deg	20.7195(14)	90.00	90.00
<i>β</i> , deg	74.412(5)	90.00	90.00
<i>γ</i> , deg	83.443(6)	90.00	90.00
<i>V</i> , Å ³	3124.4(2)	2123.38(15)	2189.81(17)
<i>Z</i>	2	4	4
<i>D</i> _c , g cm ⁻³	1.847	1.990	1.957
<i>μ</i> , mm ⁻¹	14.462	14.383	13.900
<i>F</i> (000)	1672	1216	1240
2 θ _{max} , deg	45	45	45
no. reflections	44173	13191	19234
no. independent reflections	11036 [<i>R</i> (int) = 0.0823]	3816 [<i>R</i> (int) = 0.0386]	2073 [<i>R</i> (int) = 0.0560]
no. variables	728	253	178
<i>GOF</i> on <i>F</i> ²	1.062	1.147	1.123
<i>R</i> ₁ ^{<i>a</i>}	0.0523 [<i>I</i> > 2σ(<i>I</i>)]	0.0513 [<i>I</i> > 2σ(<i>I</i>)]	0.0599 [<i>I</i> > 2σ(<i>I</i>)]
<i>wR</i> ₂ ^{<i>b</i>}	0.1394	0.1618	0.1324
residual ρ, eÅ ⁻³	+1.718, -1.956	+1.071, 1.599	+3.808, -2.593

^{*a*} $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^{*b*} $Rw = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

Table S2. Photophysical Data.

Complex	Medium (T / K)	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	$\lambda_{\text{em}} / \text{nm}$ ($\tau / \mu\text{s}$)	Φ_{em}	k_r / s^{-1}	$k_{\text{nr}} / \text{s}^{-1}$
1·Na	CH ₃ OH (298)	273 (13.4), 284 (19.5), 295 (sh) (15.7)	402, 424 (max, 0.7)	0.03	4.3×10^4	1.4×10^6
	EtOH/MeOH (77)		396, 420 (max, 15.8), 433, 46			
	Solid (298)		452 (sh), 465 (max, 2.6), 481, 491, 564			
	Solid (77)		467 (2.8)			
2·Na	CH ₃ OH (298)	239 (11.3), 306 (12.5), 309 (13.2), 319 (19.1), 322 (18.0)	425, 452 (1.3)	0.12	9.2×10^4	6.8×10^5
	EtOH/MeOH (77)		418 (16.8), 447, 460, 475, 493, 509, 528, 550, 570			
	Solid (298)		467, 483 (14.3), 529 (sh)			
	Solid (77)		515 (16.7), 535			
3·Na	CH ₃ OH (298)	217 (19.8), 231 (13.7), 258 (8.6), 268 (6.3)	Non-emissive			
4·Na	CH ₃ OH (298)	238 (16.0), 250 (12.3), 265 (12.6), 311 (23.0)	429, 455 (16.0), 498	0.13	8.1×10^3	5.4×10^4
	EtOH/MeOH (77)		428 (18.3), 442, 457, 470, 485, 501, 520, 538			
	Solid (298)		499 (17.6), 535			
	Solid (77)		471, 495 (23.4), 526			
5·PF₆	CH ₃ CN (298)	244 (10.6), 260 (10.2), 292 (25.6), 300 (24.2), 306 (22.1)	414, 438 (max, 1.4)	0.08	5.7×10^4	6.6×10^5
	EtOH/MeOH (77)		409 (12.1), 435, 448, 464 (sh), 480			
	Solid (298)		462 (sh), 467 (3.4), 480, 491, 564;			
	Solid (77)		475 (9.4), 501 (sh)			
5·Cl	CH ₃ OH (298)	243 (14.2), 256 (14.8), 290 (24.2), 298 (21.8), 303 (sh, 20.3)	414, 438 (max, 1.1)	0.08	7.3×10^4	8.4×10^5
	H ₂ O (298)	248 (11.5), 288 (17.3), 298 (14.9), 320 (tail, 2.1)	412, 437 (1.2)	0.09		
6·PF₆	CH ₃ CN (298)	245 (14.1), 313 (23.9), 322 (24.3), 330 (sh, 18.4)	429 (max, 0.5), 456	0.14	2.8×10^5	1.7×10^6
	EtOH/MeOH (77)		423 (17.8), 451, 464, 478, 495, 514			
	Solid (298)		472 (8.5), 500, 538 (sh)			
	Solid (77)		524 (10.6), 545, 585 (sh)			
6·Cl	CH ₃ OH (298)	241 (11.9), 314 (15.6), 327 (18.4), 331 (sh, 16.7)	429 (max, 0.7), 457	0.13	1.9×10^5	1.2×10^6
7·PF₆	CH ₃ CN (298)	225 (16.6), 261 (22.7), 277 (20.6), 290 (22.7)	Non-emissive			
	EtOH/MeOH (77)		398, 427 (4.5), 478			
8·PF₆	CH ₃ CN (298)	240 (14.8), 260 (13.9), 344 (34.2)	450 (5.6), 472 (sh)	0.07	1.3×10^4	1.7×10^5
	EtOH/MeOH (77)		429 (14.3), 443, 460, 473, 489, 505, 524			
	Solid (298)		525 (6.4), 563			
	Solid (77)		489 (12.4), 524, 543, 560			

Supplementary absorption and emission spectra

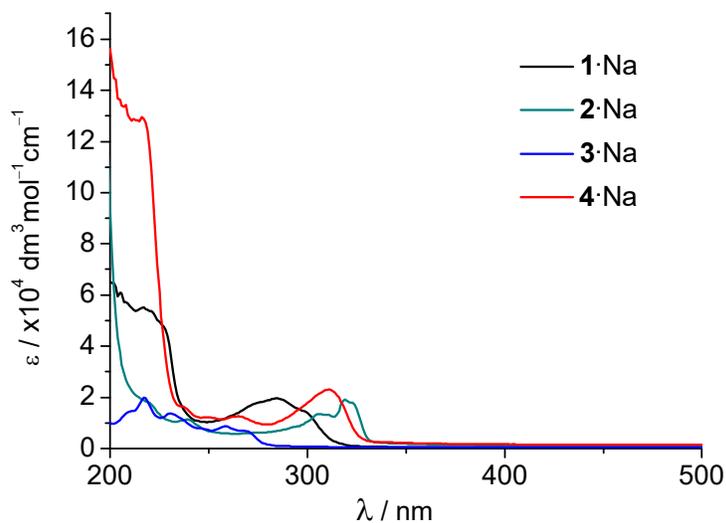


Figure S1. Electronic absorption spectra of complex **1**·Na-**4**·Na in CH₃OH at 298 K.

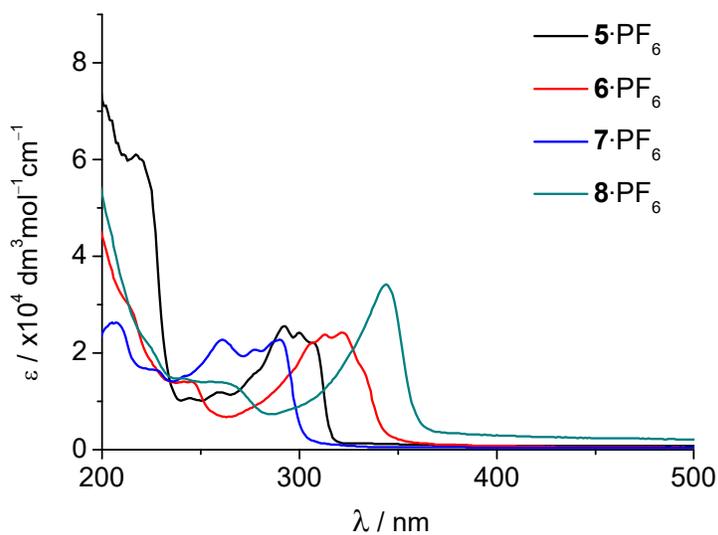


Figure S2. Electronic absorption spectra of complexes **5**·PF₆-**8**·PF₆ in CH₃CN at 298 K.

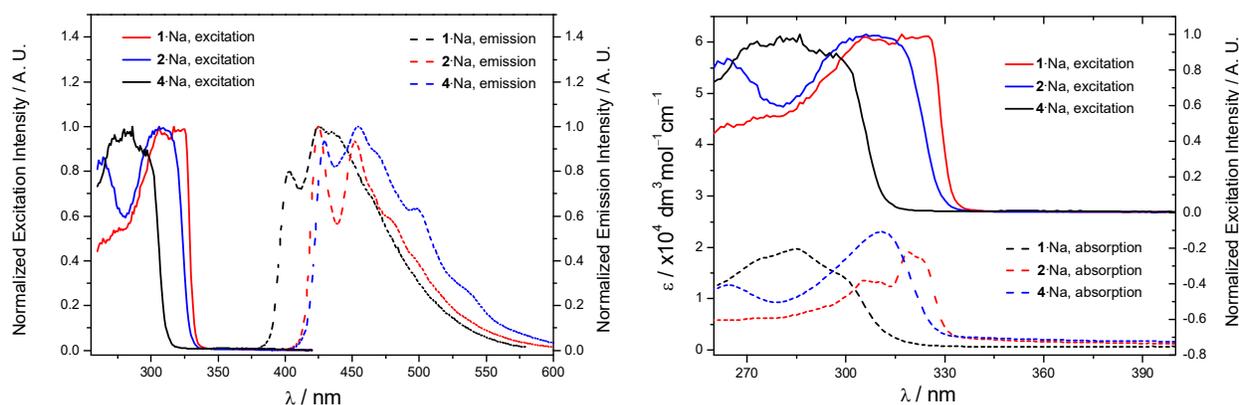


Figure S3. (Left) Normalized excitation (monitored at $\lambda_{em} = 450$ nm) and emission ($\lambda_{ex} = 300$ nm) spectra of complexes **1**·Na, **2**·Na and **4**·Na in degassed CH₃OH (concentration around 1.0×10^{-5} M) at 298 K. The slits for emission and excitation measurements are all 1 mm. (Right) The comparison between excitation and absorption spectra for complexes **1**·Na, **2**·Na and **4**·Na.

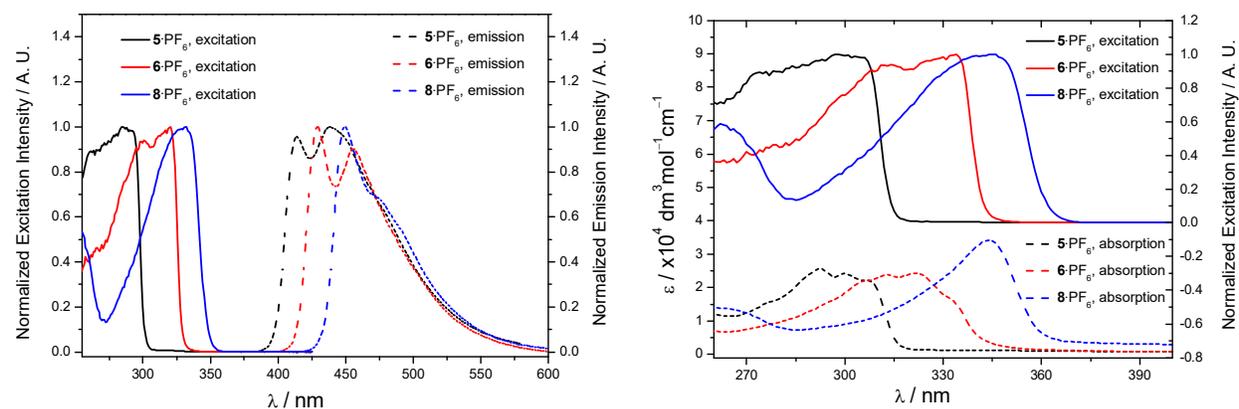


Figure S4. (Left) Normalized excitation (monitored at $\lambda_{em} = 450$ nm, 320, and 345 nm for **5**·PF₆, **6**·PF₆, and **8**·PF₆, respectively) spectra of complexes **5**·PF₆, **6**·PF₆, and **8**·PF₆ in degassed CH₃CN (concentration around 1.0×10^{-5} M) at 298 K. The slits for emission and excitation measurements are all 1 mm. (Right) The comparison between excitation and absorption spectra for complexes **5**·PF₆, **6**·PF₆, and **8**·PF₆.

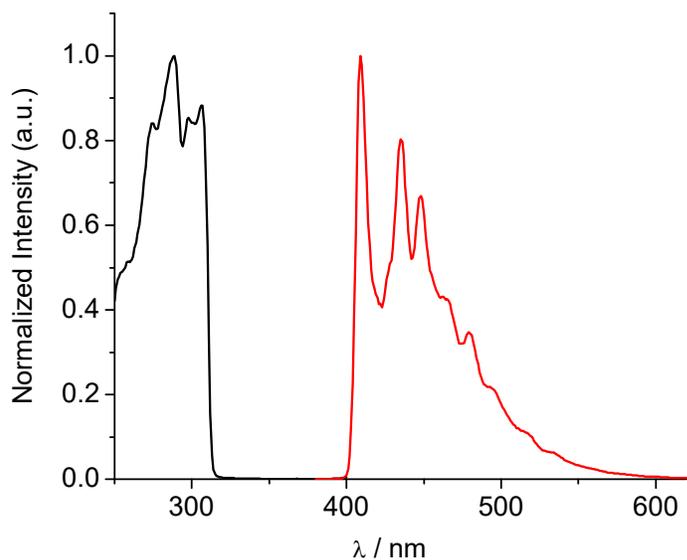


Figure S5. Excitation ($\lambda_{\text{em}} = 410$ nm) and emission ($\lambda_{\text{ex}} = 305$ nm) spectra of **5-Cl** in MeOH/EtOH (4:1, v/v) at 77 K.

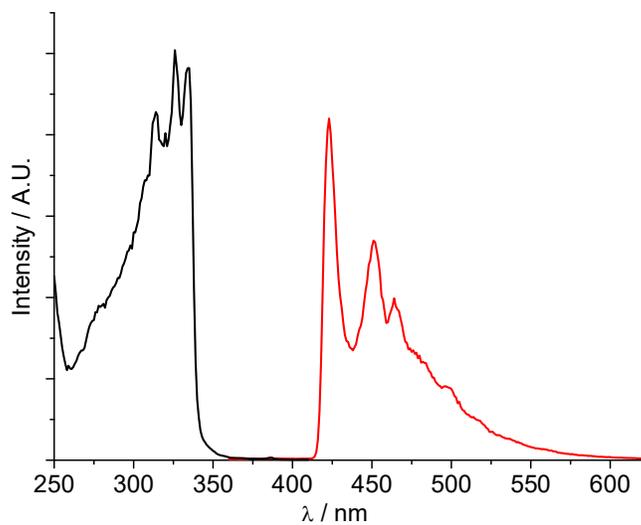


Figure S6. Excitation ($\lambda_{\text{em}} = 505$ nm) and emission ($\lambda_{\text{ex}} = 330$ nm) spectra of **6-Cl** in MeOH/EtOH (4:1) at 77 K.

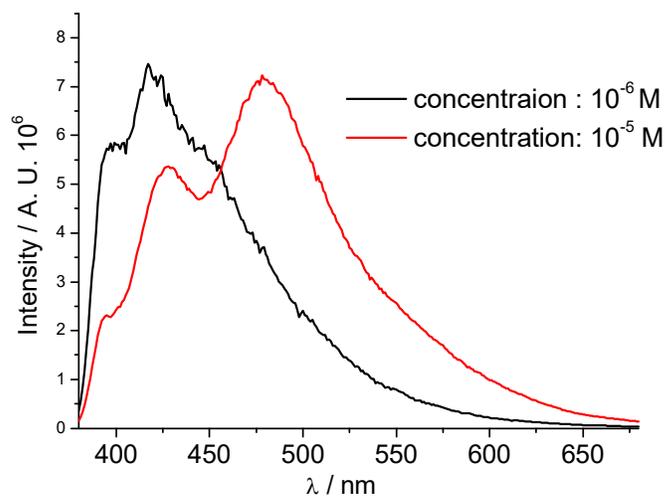


Figure S7. Emission spectra of 7·PF₆ in alcoholic glassy solution at 77 K ($\lambda_{\text{ex}} = 350$ nm).

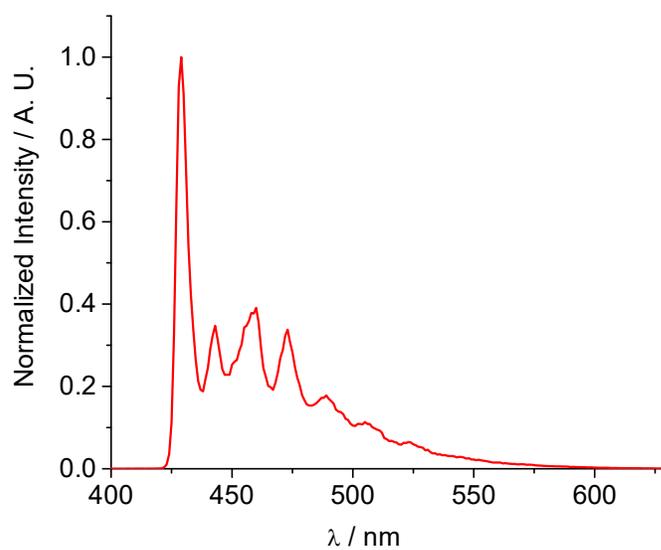


Figure S8. Emission spectra of 8·PF₆ in alcoholic glassy solutions at 77 K ($\lambda_{\text{ex}} = 340$ nm).

Supplementary time-resolved emission and transient absorption spectra

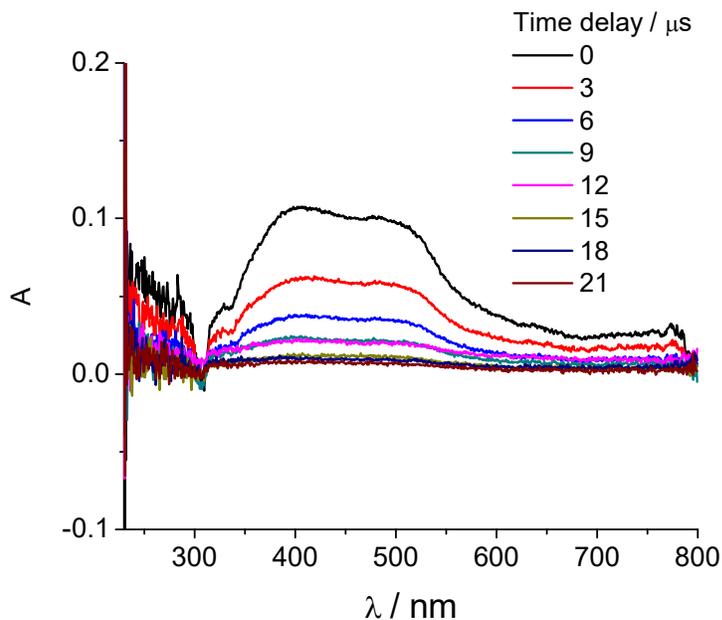


Figure S9. Transient absorption spectra at selected time decays for complex **5**·PF₆ in degassed acetonitrile at 298 K ($\lambda_{\text{ex}} = 266$ nm laser pulse).

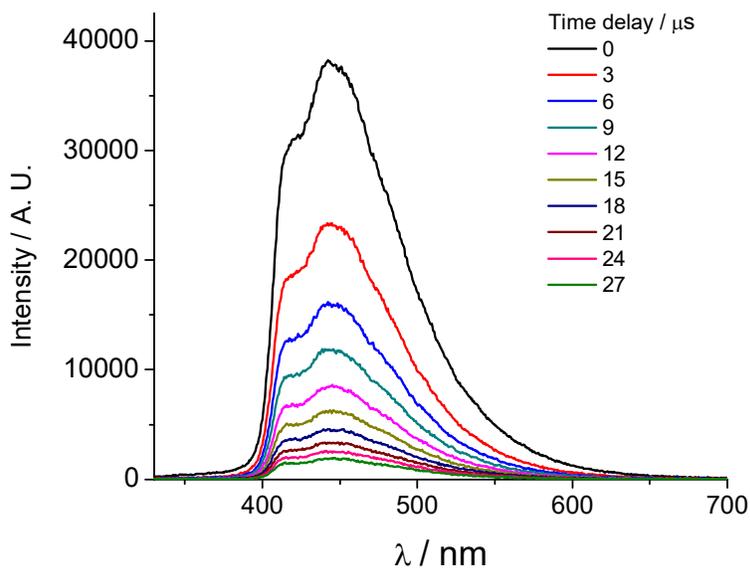


Figure S10. Time-resolved emission spectra of **5**·PF₆ in degassed acetonitrile at 298 K ($\lambda_{\text{ex}} = 266$ nm laser pulse).

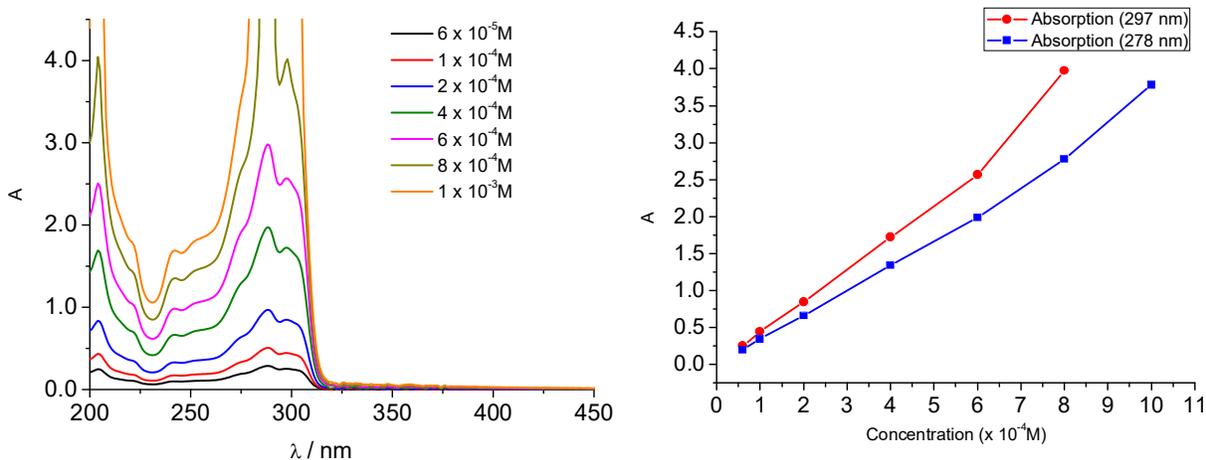


Figure S11. (Left) Variable-concentration absorption spectra of aqueous solutions of **5·Cl** at 298 K. (Right) Plot of absorbance at 297 nm and 278 nm against concentrations of aqueous solutions of **5·Cl** at 298 K.

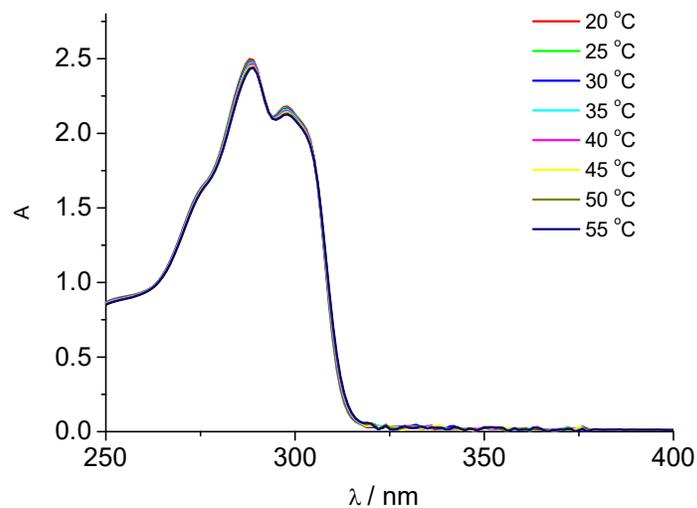


Figure S12. Absorption spectra of an aqueous solution of **5·Cl** (concentration around 5×10^{-4} M) at variable temperatures.

SEM micrograph of self-assembled nanostructures

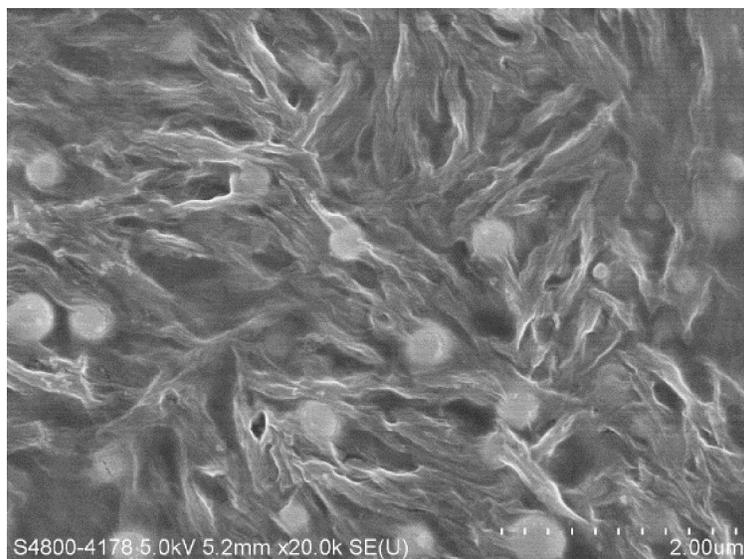


Figure S13. Scanning electron micrograph of **5·Cl** dried from chromonic aqueous solution (5.0 wt%).

DFT and TDDFT Calculations

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations have been performed to understand the geometries and the electronic structures of Au(I) allenylidene complexes (**5** and **7**) using Gaussian 09 package.^[4] M06 functional^[5] with triplet zeta basis set (6-311G* for C, H, O, N atoms, and lanl2tz for Au atoms)^[6] has been used for geometry optimization and TDDFT calculation. The Solvent effects have been studied using self-consistent reaction field (SCRF) method based on PCM models.^[7]

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- [6] (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.
- [7] (a) O. Tapia, *J. Math. Chem.*, 1992, **10**, 139; (b) J. Tomasi and M. Persico, *Chem. Rev.*, 1994, **94**, 2027.

Cartesian coordinates

5 ground state

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	79	0	-0.000523	-0.001833	-0.015233
2	6	0	-2.003841	0.013912	-0.010366
3	6	0	-3.227169	0.026153	-0.002387
4	6	0	-4.612963	0.009403	0.008542
5	7	0	-5.390718	-1.093376	-0.034482
6	6	0	-4.871642	-2.448523	-0.123690
7	1	0	-4.124361	-2.608632	0.656009
8	1	0	-4.407964	-2.610780	-1.099678
9	1	0	-5.696317	-3.148566	0.011331
10	6	0	-6.713583	-0.716510	-0.008309
11	1	0	-7.511912	-1.442873	-0.037457
12	6	0	-6.745742	0.633714	0.054888
13	1	0	-7.576814	1.321885	0.095596
14	7	0	-5.441291	1.074340	0.063863
15	6	0	-5.014432	2.461493	0.134251
16	1	0	-5.313718	2.896463	1.090515
17	1	0	-5.463281	3.027244	-0.684847

18	1	0	-3.927723	2.494524	0.045770
19	6	0	2.002926	-0.015781	-0.013517
20	6	0	3.226248	-0.023642	-0.008009
21	6	0	4.612253	-0.005762	0.000761
22	7	0	5.392442	1.094897	-0.056914
23	6	0	4.883547	2.455696	-0.104866
24	1	0	3.997378	2.486179	-0.740881
25	1	0	4.614877	2.796586	0.898086
26	1	0	5.653942	3.106046	-0.520514
27	6	0	6.714606	0.715932	-0.016584
28	1	0	7.514099	1.440832	-0.050735
29	6	0	6.743968	-0.633467	0.059966
30	1	0	7.573549	-1.323280	0.103830
31	7	0	5.438666	-1.071547	0.069124
32	6	0	5.010078	-2.458170	0.141100
33	1	0	5.437504	-3.021053	-0.691400
34	1	0	5.331325	-2.898493	1.087696
35	1	0	3.921536	-2.488135	0.078302

5 Triplet excited state

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-1.949325	-0.078237	-0.044626
2	6	0	-3.201077	-0.081030	-0.043892
3	79	0	0.000222	-0.075101	-0.049569
4	6	0	1.949773	-0.074871	-0.054280
5	6	0	3.201516	-0.077675	-0.056038
6	6	0	-6.688873	0.585771	-0.064719
7	6	0	-6.682600	-0.778684	-0.030029
8	1	0	-7.519539	1.276104	-0.086024
9	1	0	-7.506920	-1.476631	-0.010288
10	6	0	6.689720	0.587287	-0.046016
11	6	0	6.682632	-0.777506	-0.064447
12	1	0	7.520795	1.277339	-0.033624
13	1	0	7.506548	-1.476147	-0.076235
14	7	0	-5.385147	-1.192899	-0.021697
15	7	0	-5.395179	1.011950	-0.070403
16	7	0	5.384944	-1.191017	-0.066965
17	7	0	5.396274	1.014238	-0.043780
18	6	0	-4.556433	-0.086639	-0.045212
19	6	0	4.556876	-0.084054	-0.055777
20	6	0	-4.897438	-2.553898	0.043668
21	1	0	-4.179336	-2.730007	-0.761471
22	1	0	-4.401957	-2.734487	1.002394

23	1	0	-5.739542	-3.238078	-0.064831
24	6	0	-4.919810	2.377398	-0.134206
25	1	0	-4.206652	2.560274	0.673879
26	1	0	-4.422071	2.562405	-1.090993
27	1	0	-5.768677	3.053786	-0.029355
28	6	0	4.896527	-2.552445	-0.115568
29	1	0	4.178239	-2.718166	0.691561
30	1	0	4.401097	-2.744683	-1.072038
31	1	0	5.738224	-3.235695	0.001534
32	6	0	4.921556	2.380651	0.000748
33	1	0	4.221369	2.558061	-0.819747
34	1	0	4.409350	2.573847	0.948047
35	1	0	5.772879	3.055078	-0.095987

7 ground state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.000165	-0.394126	-0.088189
2	6	0	3.222348	-0.416503	-0.145999

3	6	0	4.611463	-0.472734	-0.229598
4	8	0	5.253820	-1.554839	-0.601428
5	7	0	5.369566	0.558208	0.058888
6	6	0	4.849666	1.856861	0.519017
7	1	0	4.083631	1.703056	1.284010
8	1	0	4.381885	2.373516	-0.329333
9	6	0	4.495783	-2.724315	-0.946563
10	1	0	3.885028	-3.041646	-0.098746
11	1	0	5.237300	-3.482342	-1.189440
12	1	0	3.859092	-2.519057	-1.809782
13	6	0	7.189807	2.025239	0.085854
14	1	0	8.200727	2.175288	0.471839
15	1	0	7.133020	2.512601	-0.895350
16	6	0	6.102790	2.564189	1.007252
17	1	0	6.311510	2.283164	2.046987
18	1	0	6.002491	3.651315	0.971494
19	6	0	6.838774	0.552481	-0.045159
20	1	0	7.146973	0.092464	-0.987463
21	1	0	7.250932	-0.050576	0.774183
22	79	0	0.000014	-0.382572	0.000047
23	6	0	-2.000144	-0.394253	0.088107
24	6	0	-3.222350	-0.416551	0.145458
25	6	0	-4.611444	-0.472756	0.229441

26	8	0	-5.253718	-1.554825	0.601510
27	7	0	-5.369605	0.558177	-0.058929
28	6	0	-4.495625	-2.724300	0.946521
29	6	0	-4.849793	1.856778	-0.519292
30	6	0	-6.838788	0.552485	0.045475
31	1	0	-3.885188	-3.041776	0.098526
32	1	0	-5.237094	-3.482256	1.189763
33	1	0	-3.858607	-2.518972	1.809480
34	1	0	-4.083898	1.702894	-1.284409
35	1	0	-4.381863	2.373506	0.328923
36	6	0	-6.103015	2.564052	-1.007357
37	6	0	-7.189850	2.025227	-0.085673
38	1	0	-7.146771	0.092605	0.987923
39	1	0	-7.251149	-0.050687	-0.773685
40	1	0	-6.311943	2.282914	-2.047015
41	1	0	-6.002705	3.651175	-0.971739
42	1	0	-8.200848	2.175228	-0.471471
43	1	0	-7.132863	2.512717	0.895457

7 Triplet excited state

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	1.946960	0.459292	-0.009009
2	6	0	3.199161	0.468365	-0.015305
3	6	0	4.574322	0.493557	-0.020361
4	8	0	5.300621	1.604214	-0.049717
5	7	0	5.301308	-0.633521	0.007779
6	6	0	4.731926	-1.981964	0.013577
7	1	0	3.903748	-2.048265	-0.698252
8	1	0	4.330511	-2.199140	1.014598
9	6	0	4.610002	2.853096	-0.073504
10	1	0	3.972646	2.921460	-0.959714
11	1	0	5.386023	3.615229	-0.108866
12	1	0	4.002984	2.972681	0.828366
13	6	0	7.089782	-2.105010	0.323056
14	1	0	8.067091	-2.394960	-0.069420
15	1	0	7.101715	-2.279814	1.405980
16	6	0	5.930354	-2.854427	-0.320684
17	1	0	6.064469	-2.904899	-1.408286
18	1	0	5.813757	-3.876069	0.048090
19	6	0	6.764350	-0.648082	0.036679
20	1	0	7.136430	0.061199	0.782782
21	1	0	7.144561	-0.316737	-0.941458
22	79	0	0.000000	0.454210	-0.000019

23	6	0	-1.946959	0.459294	0.008989
24	6	0	-3.199163	0.468372	0.015331
25	6	0	-4.574325	0.493561	0.020388
26	8	0	-5.300625	1.604220	0.049757
27	7	0	-5.301308	-0.633522	-0.007756
28	6	0	-4.610010	2.853104	0.073542
29	6	0	-4.731924	-1.981965	-0.013563
30	6	0	-6.764349	-0.648090	-0.036657
31	1	0	-3.972640	2.921462	0.959742
32	1	0	-5.386032	3.615235	0.108924
33	1	0	-4.003007	2.972697	-0.828337
34	1	0	-3.903744	-2.048267	0.698263
35	1	0	-4.330510	-2.199131	-1.014587
36	6	0	-5.930347	-2.854435	0.320693
37	6	0	-7.089777	-2.105018	-0.323039
38	1	0	-7.136431	0.061193	-0.782755
39	1	0	-7.144558	-0.316750	0.941482
40	1	0	-6.064460	-2.904915	1.408296
41	1	0	-5.813747	-3.876075	-0.048087
42	1	0	-8.067085	-2.394974	0.069437
43	1	0	-7.101712	-2.279818	-1.405964
