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Different Structures Modulated Mechanochromism and Aggregation-induced Emission in a series of Gold(I) Complexes

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Hua Liu^{a,b,*}

Graphical Abstract

Five novel gold(I) complexes with distinct diverse (bicolor or tricolor) switching mechanochromic and prominent AIE properties have been reported in present work. Abnormally, the *e*- and *a*-conformers coexisted in the same crystal unit cell for mono-substituted cyclohexyl Au(I) complex, which is quite rare in the similar gold systems. The five newly-developed(I) complexes are anticipated to be used as fluorescent detector and mechanosensors.



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2	Aggregation-induced Emission in a series of Gold(I) Complexes
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12	
13	ABSTRACT
14	Five novel gold(I) complexes with various isocyanide ligands have been synthesized and
15	characterized in present work. The introduction of different terminal ligands endows
16	distinct diverse properties to complexes 1-5: i) alkyl modified complexes 1-3 exhibit
17	tricolor or bicolor mechanochromic behaviors due to the loosing packing formed through

weak intermolecular C-H···F interactions, while aryl bridged complexes 4 and 5 are not

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19	mechano-responsive with tight π - π stackings; ii) all the target complexes present
20	prominent but different aggregation-induced emission(AIE) characteristics caused by the
21	inherent difference in their structures. Therefore, the above gold(I) complexes are
22	anticipated to be used as fluorescent detectors and mechanosensors.
23	Key words: Gold(I)-isocyanide complexes; Mechanochromism; Aggregation-induced
24	emission(AIE); Crystal structures
25	1. Introduction
26	Smart materials refer to the materials that can make response upon external (optical,
27	electrical, thermal, solvent, anions, mechanical, etc.) stimulation [1-6].
28	Mechanical-responsive luminescent materials, as one of quintessential representatives of
29	smart materials, have attracted increasing attention because of their extensive
30	applications in optoelectronic devices [7], storage and memories fields [8], mechanical
31	sensors [6], and chemical detectors [9]. The solid-state luminance of mechanochromic
32	materials usually exhibit reversible or irreversible turn-on switching [4], or turn-off

switching [5] involving two-color transformation [6], or even multicolor tunning [7, 10]

under the stimuli of mechanical force (press, shear, stretch, grind, etc [6, 7,10-11]).

Among them, metal complexes based on Pt(II) [13-15], Ir(III) [16-18], and Cu(I) [19-21]

constitute a significant portion, while the newly-developed systems associated with Au(I)

are still limited in recent years [22-26]. In 2008, the first gold(I) complex that exhibits

blue-to-yellow emission conversion upon grinding with pestle was reported by Ito and
co-workers [22]. The related research results indicate that intermolecular aurophilic
interactions may be the main reason for the emission change upon mechanic stimulation.
However, multicolor mediated mechanochromic materials are very rare, let alone the
capture of the unstable intermediate state before recovering to initial state [27].
In the meanwhile, the development of luminogens with aggregation-induced
emission characteristic (AIEgens) has been in a boiling state since the discovery of

abnormal AIE phenomenon by Tang's group in 2001 [28]. So far, a great number of gold 45 complexes with AIE or mechanochromic properties have been reported [29-38]. In our 46 previous work, we also developed a series of gold(I)-isocyanide complexes exhibiting 47 outstanding AIE and mechanochromic behaviors [24, 25, 39], in which the Au-C≡N 48 coordination bonds are linear or approximately linear similar to the other reported gold(I) 49 isocyanide complexes. In this paper, we reported five novel gold(I) complexes with 50 different isocyanide ligands (Figure 1) and investigated thoroughly the effect of terminal 51 ligands on photophysical properties of these gold(I) complexes. In addition, we observed 52 some significant conformations according to our following crystal analysis. The above 53 special structural characteristics may endow these systems distinct photophysical 54 properties. 55

Insert Figure 1

57 2. Experiments

58 2.1. Materials and methods

Specific synthetic strategy has been demonstrated in Scheme 1. All manipulations 59 were carried out under an argon atmosphere by using standard Schlenk techniques, 60 unless otherwise stated. The starting material isocyanide 1a, 2a, 3a, 4a were 61 purchased from Alfa Aesar and were used directly. CH₂Cl₂ was dried with CaH₂ 62 then distilled, and ultra-pure water was used in the experiments. All other starting 63 materials and reagents were obtained commercially from Shen Shi Hua Gong 64 Company (China) as analytical-grade and used without further purification. ¹H 65 NMR and ¹³C NMR spectra were collected on American Varian Mercury Plus 400 66 spectrometer (400 MHz), Bruker AVANCE III HD-400 or Varian MERCURY Plus 67 600 MHz instrument. ¹H NMR spectra are reported as followed: chemical shift in 68 ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities 69 (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constant (Hz). ^{13}C 70 NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for 71 CDCl₃ at 77 ppm. ¹⁹F NMR chemical shifts are relative to C₆F₆ (δ = -163.00). EI-MS 72 was obtained using Thermo scientific DSQ . Elemental analyses (C, H, N) were 73 performed by the Microanalytical Services, College of Chemistry, CCNU. UV-Vis 74 spectra were obtained on Shimadzu UV-3600 spectrophotometer. Fluorescence 75 spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer and 76 Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.) Absolute 77

78	fluorescence quantum yields were measured on a Hamamatsu C11347 Absolute PL
79	quantum yield spectrometer. XRD studies were recorded on a Shimadzu XRD-6000
80	diffractometer using Ni-filtered and graphite-monochromated Cu K α radiation (λ =
81	1.54 Å, 40 kV, 30 mA). The X-ray crystal-structure data were obtained by the
82	Bruker APEX DUO CCD system. DFT calculations were performed with the
83	Gaussian 09 program at the B3LYP/6-31G* (Au: Lanl2DZ) level of theory.
84	2.2. Synthesis
85	2.2.1. General procedure for the synthesis of 4b-4c
86	Compounds 4b , 4c , $Au(C_6F_5)(tht)$ (tht = tetrahydrothiophene) were prepared
87	according to the corresponding literatures [40-42]. 4b: Yield: 73%. ¹ H NMR (600 MHz,
88	DMSO- d^{6}): δ (ppm) = 10.31 (s, 1H, CHO), 8.48 (s, 1H, NH), 8.13 (d, $J = 8.4$ Hz, 1H,
89	Ar- <i>H</i>), 8.07-7.86 (m, 2H, Ar- <i>H</i>), 7.76 (m, 1H, Ar- <i>H</i>), 7.52 (d, <i>J</i> = 47.2 Hz, 3H, Ar- <i>H</i>).
90	EI-MS: $m/z = 171.2$ [M] ⁺ ; Found: $m/z = 171.2$ [M] ⁺ . 4c: Yield: 50%. ¹ H NMR (400
91	MHz, CDCl ₃): δ (ppm) = 8.19 (d, <i>J</i> = 8.4 Hz, 1H, Ar- <i>H</i>), 7.89 (d, <i>J</i> = 8.4 Hz, 2H, Ar- <i>H</i>),
92	7.67 (d, <i>J</i> = 8.3 Hz, 1H, Ar- <i>H</i>), 7.58-7.62 (m, 2H, Ar- <i>H</i>), 7.44 (d, <i>J</i> = 8.2 Hz, 1H, Ar- <i>H</i>).
93	EI-MS: $m/z = 153.2$ [M] ⁺ ; Found: $m/z = 153.3$ [M] ⁺ .

94 2.2.2. General procedure for the synthesis of **5b-5d**

Syntheses of compounds 5b and 5c: The mixture of 5a (0.50 g, 2.60 mmol) and
K₂CO₃ (1.10 g, 7.80 mmol) was added in DMF (30 ml). And 1-bromodecane (0.69 g,
3.10 mmol) was added dropwise after heating to reflow temperature and the reaction

solution was refluxed for 12 hours. Then the reaction system was extracted with CH₂Cl₂ 98 (3×20 mL). The combined organic layer was dried over anhydrous magnesium sulfate, 99 filtered and concentrated under reduced pressure to afford a deep purple oily liquid. The 100 residue was stirred for 12 h at 110 \square with formic acid (30 ml). After a series of 101 post-processing, collecting the expected purple solid 0.41 g of 5c in a yield of 48%. ¹H 102 NMR (400 MHz, CDCl₃): δ (ppm) = 8.41 (d, J = 11.5 Hz, 0.5 H, CHO, *cis*), 8.34 (d, J = 103 8.2 Hz, 0.5 H, CHO, trans), 7.90 (d, J = 8.3 Hz, 0.5 H, NH, trans), 7.72-7.81 (dd, J = 8.3 104 Hz, 0.5 H, NH, *cis*), 7.61 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.56 (t, *J* = 13.5 Hz, 1H, Ar-*H*), 7.26 105 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.23 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 6.78 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 106 4.14 (t, J = 6.3 Hz, 2H, OCH₂), 1.93 (d, J = 6.9 Hz, 4H, CH₂), 1.35 (s, 12H, CH₂), 0.88 (t, 107 J = 6.5 Hz, 3H, CH₃). EI-MS: m/z = 327.5 [M]⁺; Found: m/z = 327.3 [M]⁺. 108

109 Synthesis of compound **5d**: The procedure of **5d** is similar to compound **4c** using the 110 following amounts: **5c** (1.00 g, 5.80 mmol) and triphosgene (1.89 g, 6.40 mmol). The 111 product was obtained as a deep purple solid (0.42 g) in a yield of 64%. ¹H NMR (400 112 MHz, CDCl₃): δ (ppm) = 8.32 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 8.12 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 113 7.68 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.60 - 7.51 (m, 2H, Ar-*H*), 6.72 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 114 4.16 (t, *J* = 6.4 Hz, 2H, OCH₂), 2.22 - 1.94 (m, 4H, CH₂), 1.27 (d, *J* = 9.3 Hz, 12H, CH₂), 115 0.88 (t, *J* = 7.0 Hz, 3H, CH₃). EI-MS: *m/z* = 309.5 [M]⁺; Found: *m/z* = 309.6 [M]⁺.

116 2.2.3. General procedure for the synthesis of 1-5

117	Synthesis of complex 1: Under an argon atmosphere, a mixture of $C_6F_5Au(tht)$ (0.41)
118	g, 0.91 mmol) and 1a (0.074 g, 0.88 mmol) was stirred in CH ₂ Cl ₂ (20 ml) overnight at
119	room temperature. After finishing the present reaction, the reaction system was
120	concentrated in vacuo. Recrystallization with CH ₂ Cl ₂ /n-hexane. The product was
121	obtained as a light-yellow solid (0.20 g, 52%). ¹ H NMR (400 MHz, CDCl ₃): δ (ppm) =
122	1.61 (s, 9H, CH ₃). ¹³ C NMR (100 MHz, CDCl ₃): δ (ppm) = 150.5, 148.5, 140.5, 138.1,
123	135.7, 58.7, 29.7. ¹⁹ F NMR (CDCl ₃): δ (ppm) = -116.1, -157.9, -162.8. IR (KBr): 2219
124	$v(C=N) \text{ cm}^{-1}$. Anal. Calcd for C ₁₁ H ₉ AuF ₅ N: C, 29.55; H, 2.03; N, 3.13. Found: C, 29.34;
125	H, 2.13; N, 3.09.

Synthesis of complex 2: The procedure of complex 2 is similar to complex 1 using 126 the following amounts: $C_6F_5Au(tht)$ (0.46 g, 1.03 mmol) and **2a** (0.11 g, 1.00 mmol). 127 The product was obtained as a white solid product (0.47 g, 46%). ¹H NMR (400 MHz, 128 CDCl₃): δ (ppm) = 3.89 (s, 1H, NCH), 2.03 (s, 2H, CH₂), 1.81 (s, 4H, CH₂), 1.48 (s, 4H, 129 CH₂). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.7, 149.1, 148.2, 140. 5, 138.0, 135.6, 130 128.4, 54.7, 31.6, 24.6, 22.7. ¹⁹F NMR (CDCl₃): δ (ppm) = -115.9, -158.1, -162.7. IR 131 (KBr): 2217 $v(C \equiv N)$ cm⁻¹. Anal. Calcd for C₁₃H₁₁AuF₅N: C, 33.00; H, 2.34; N, 2.96. 132 Found: C, 32.88; H, 2.42; N, 2.90. 133

134 Synthesis of complex **3**: The procedure of complex **3** is similar to complex **1** using 135 the following amounts: $C_6F_5Au(tht)$ (0.46 g, 1.03 mmol) and **3a** (0.13 g, 1.00 mmol). The 136 product was obtained as a white solid (0.27 g, 56%). ¹H NMR (400 MHz, CDCl₃): δ

137	(ppm) = 7.36 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.19 (d, $J = 7.7$ Hz, 2H,	Ar- <i>H</i>), 2.50 (s, 6H,
138	Ar-CH ₃). ¹³ C NMR (100 MHz, CDCl ₃): δ (ppm) = 161.0, 150.5,	148.2, 140.6, 138.1,
139	136.2, 131.0, 128.5, 124.1, 18.7. ¹⁹ F NMR (CDCl ₃): δ (ppm) = -116	.0, -157.5, -162.5. IR
140	(KBr): 2220 $v(C=N)$ cm ⁻¹ . Anal. Calcd for C ₁₅ H ₉ AuF ₅ N: C, 36.3	8; H, 1.83; N, 2.83.
141	Found: C, 36.27; H, 1.91; N, 2.76.	

Synthesis of complex 4: The synthesis of complex 4 is similar to complex 1 using 142 the following amounts: $C_6F_5Au(tht)$ (0.29 g, 0.44 mmol) and 4c (0.07 g, 0.43 mmol). The 143 product was obtained as a white solid (0.13 g, 58%). ¹H NMR (400 MHz, CDCl₃): δ 144 (ppm) = 8.12 (t, J = 9.0 Hz, 2H, Ar-H), 8.00 (d, J = 7.9 Hz, 1H, Ar-H), 7.85 - 7.75 (m, 145 2H, Ar-H), 7.71 (t, J = 7.1 Hz, 1H, Ar-H), 7.57 (t, J = 8.4 Hz, 1H, Ar-H). ¹³C NMR (100 146 MHz, CDCl₃): δ (ppm) = 133.6, 132.3, 129.2, 128.9, 128.3, 127.7, 126.2, 125.0, 121.9. 147 ¹⁹F NMR (CDCl₃): δ (ppm) = -116.0, -157.3, -162.3. IR (KBr): 2220 ν (C=N) cm⁻¹. Anal. 148 Calcd for C₁₇H₇AuF₅N: C, 39.48; H, 1.36; N, 2.71. Found: C, 39.35; H, 1.45; N, 2.65. 149

Synthesis of complex **5**: The procedure of **5** is similar to complex **1** with C₆F₅Au(tht) (0.20 g, 0.45 mmol) and **5d** (0.14 g, 0.44 mmol). The product was obtained as a white solid (0.19 g, 65%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.39 (d, *J* = 9.0 Hz, 1H, Ar-*H*), 8.03 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.83-7.70 (m, 2H, Ar-*H*), 7.65 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 6.80 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 4.21 (t, *J* = 6.4 Hz, 2H, OCH₂), 2.03 -1.90 (m, 2H, CH₂), 1.46 - 1.18 (m, 14H, CH₂), 0.89 (t, *J* = 7.0 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 159.6, 158.0, 150.8, 148.5, 140.6, 138.2, 135.7, 129.4,

157	128.7, 127.5, 125.6, 123.3, 121.7, 113.0, 103.6, 69.2, 31.9, 29.6, 29.3, 29.0, 26.2, 22.7,
158	14.1. ¹⁹ F NMR (CDCl ₃): δ (ppm) = -116.0, -157.6, -162.4. IR (KBr): 2222 v(C≡N) cm ⁻¹ .
159	Anal. Calcd for C ₂₇ H ₂₇ AuF ₅ NO: C, 48.15; H, 4.04; N, 2.08. Found: C, 48.03; H, 4.11; N,
160	1.99.
161	Insert Scheme 1
162	3. Results and discussion
163	3.1. Synthesis
164	The synthetic route of complexes 1-5 has been presented in Scheme 1. These five
165	target gold(I) complexes were obtained in a few steps with the yields of 46%-65%.
166	3.2. Diverse mechanochromic properties of 1-3
167	Mechanochromic properties were investigated by means of photoluminescence (PL)
168	spectroscopy. Complex 1 exhibited a "turn-on" and tricolor change in response to the
169	external mechanical stimuli. As shown in Figure 2, the initial powder of complex 1
170	exhibited a weak emission at 465 nm, which is hard to be observed under the irradiation
171	of 365 nm UV lamp due to a low quantum yield (Φ_F) of 3.7%. But its emission could be
172	further lighted up by the stimulation of mechanical force, showing bright cyan
173	luminescence with a red-shifted band at 495 nm, and the corresponding quantum yield
174	was increased by 6.5-fold ($\Phi_F = 24.2\%$). Interestingly, unlike some similar reported
175	mechanochromic systems [43], in which the emission of ground powder could revert to
176	the original state very directly after exposing to dichloromethane vapor, yet the cyan

fluorescence of complex 1 transformed into dark yellow after fuming showing a broad 177 band at around 560 nm. The above transformation between the yellow transition state and 178 the cyan state is reversible, while the original blue state could not be recovered. 179 Regarding complex 2, a reversible color change from blue ($\lambda_{em,max}$ = 466 nm) to cyan 180 $(\lambda_{em.max} = 484 \text{ nm})$ was discovered upon grinding with an obviously increased quantum 181 yield from 6.3% to 10.9%. Interestingly, we observed that the above cyan powder need 182 go through an orange transition state before recovering to the initial blue state after 183 184 fuming with dichloromethane vapor. Subsequently, this metastable state self-recovered to the original state within a few minutes without any treatment and this self-recovery 185 process showed desirable repeatability. Unfortunately, this special state was too 186 instantaneous to be further explored. In the case of complex 3, a reversible transformation 187 from an original blue emission ($\Phi_F = 27.7\%$) to a brighter cyan state ($\Phi_F = 61.3\%$) could 188 also be realized by mechanical grinding and dichloromethane fuming. Accordingly, 189 complex 3 showed a typical bicolor switching mechanochromic behavior. The detailed 190 mechanochromic data of complexes 1-3 have been summarized in Table 1. Indeed, no 191 any obvious emission change could be observed upon mechanical stimulation for 192 complexes 4 and 5. This might be caused by the existence of strong intermolecular 193 interactions and hence formed compact packings due to the presence of naphthalene rings 194 (vide infra), which is difficult to destroyed under the stimulation of external mechanical 195 forces. 196

199

Insert Figure 2

Insert Figure 3

200	To further explore the mechanochromic mechanism, the changes of molecular
201	arrangements in different states were investigated via powder X-ray diffraction (XRD).
202	As shown in Figure 2, Figure S4 and S5, the XRD patterns of the initial solid samples for
203	complexes 1–3 all exhibited sharp and intense peaks consistent with the diffraction peaks
204	obtained by single crystal structure simulation, indicating that all the original states are
205	crystalline states. After grinding with pestle, weak and broadening peaks were observed
206	for these three complexes, corresponding to the formation of amorphous phases.
207	Differently, some new ordered intense diffraction peaks differing from the initial pattern
208	appeared in complex 1 after treating the ground samples with CH_2Cl_2 vapor. The above
209	observations demonstrate that the crystalline phase after fuming is different from that of
210	unground sample and diverse morphologies give rise to various fluorescence. This may
211	be the reason why complex 1 exhibits tricolor-changing mechanochromic behavior.
212	While the reflection peaks of fumed sample could be restored for complex 2 and 3 . It
213	explained reversible bicolor but not tricolor mechanochromism for complex 2 and 3.
214	Anyway, we can preliminarily conclude that the reversible conversions between
215	crystalline states and amorphous phases are responsible for the above color changes for
216	complexes 1–3 upon mechanical stimulation.

217 3.3. Crystal structures and DFT calculations

Furthermore, we look forward to setting up deep understanding of the 218 aforementioned mechanochrmic behaviors. Fortunately, we obtained the crystal 219 structures for all the target complexes 1–5 by slow crystallization from CH₂Cl₂/MeOH 220 or hexane. Accordingly, we carried out detailed exploration for the above crystal 221 structures and anticipated to unearth some interesting information. Pertinent diffraction 222 parameters, bond lengths (Å) and bond angles (deg) have been presented in Table S1-S6 223 (ESI[†]). By comparing the above crystal data, we can observe that the whole molecular 224 skeletons of complexes 1 and 3 feature desirable coplanar and linear structure with the 225 Au–C=N and C–Au–C angles of 180.00°. The structure of complex 5 is approximately 226 linear with the Au−C≡N angle of 178.09° and C−Au−C angle of 179.73°, respectively 227 (Figure S6). The characters of the above complexes are very similar to the systems 228 reported in literatures [6, 12, 22, 23]. In addition, the nearly linear Au-C=N 229 (e-conformer: 179.57°; a-conformer: 176.93°) and C-Au-C (e-conformer: 176.37°; 230 a-conformer: 173.92°) angles in these two conformers show slightly difference for 231 complex 2. Specifically, complex 4 exhibits bent structures with the Au–C=N and 232 C-Au-C angles of 164.57° and 173.64°, respectively (Figure 5). It should be mentioned 233 that the above bending conformation is still rarely observed in the reported 234 gold(I)-isocyanide systems [6, 12, 23]. Mono-substituted cyclohexyl undergo rapid 235 chair-to-chair conversion between two different conformations, viz. equatorial (e-) and 236 axial (a-) conformers, at room temperature [44]. It has been documented that the 237 equatorial conformer is ordinarily more stable when the substituent is a bulky group due 238

to the steric effects. However, we observed both the e- and a-conformers in the same unit 239 cell for complex 2, with the isocyano-Au segment located in the equatorial and axial sites 240 on the cyclohexyl ring, respectively (Figure 4). More interestingly, the two conformers 241 are oriented in opposite directions and weak C-H···F interactions could be observed 242 between different conformers. In 2005, Balch et al. also reported a similar [(cyclohexyl 243 isocyanide)₂Au^I](PF₆) complex and they obtained the yellow and colorless forms of 244 polymorphs successfully, in which the colorless polymorph consists of two half-cations 245 with the e- and a-conformer, respectively [45]. In order to get insight into the above 246 phenomenon, we carried out the density functional theory (DFT) calculations based on 247 the monomer (e- and a-conformer) and dimer models using the B3LYP functional. The 248 basis set employed here is 6-31G* (Lanl2DZ for Au atom). As shown in Figure 6, the 249 HOMO and LUMO orbitals of both e- and a-conformers predominantly localize on the 250 C_6F_5 unit and the central isocyano-Au fragment, respectively, indicating an 251 intramolecular ligand to metal charge transfer transition character, while the two 252 monomers separately contribute to the frontier molecular orbital for the dimer and an 253 obvious intermolecular charge transfer could occur. In addition, the energies of HOMO 254 (e-: -6.06, a-: -6.08 eV) and LUMO (e-: -1.29 eV, a-: -1.36 eV) orbitals for both e- and 255 a-conformers are very similar. But their respective energy gap (-4.7 eV) is obviously 256 higher than that of the dimer (-4.3 eV). These results imply that the intermolecular charge 257 transfer is much easier to occur than that of the intramolecular process, which might 258 provide a good foundation for the stable coexistence of both two conformers. 259

Insert Figure 4

Insert Figure 5

262

Insert Figure 6

We are then interested in exploring the crystal packing of complexes 1-5 and 263 attempt to find the reason for their different mechanochromic behaviors. Complexes 1-3 264 only feature multiple intermolecular C-H···F interactions formed by head-to-tail 265 266 arrangement between the terminal penta-fluorophenyl group and the adjacent alkyl or aryl group, respectively, except for complex 3 interacting with disordered methanol 267 molecule. And these multiple intermolecular C-H...F interactions act as guiding force 268 269 and hold the molecules to form loose 3D networks for complexes 1-3. The slippage is 270 very likely to take place between molecules under the stimulus of external mechanical force and the intermolecular distances containing gold-gold distances could be perturbed, 271 which is supported by an obvious red shift in their respective emission peak after 272 grinding. By contrast, the distances between the centers of intermolecular aryl rings for 273 complexes 4 and 5 are 3.467Å and 3.472Å, respectively. It's clear that complexes 4 and 5 274 exhibited strong intermolecular π - π interactions due to the presence of naphthalene rings 275 and presented very tight stackings, which brings out that the corresponding packing 276 modes for complexes 4 and 5 are hard to change by grinding and complexes 4 and 5 277 accordingly do not show mechanochromic behaviors. In addition, based on the different 278 279 crystal packings of complexes 4 and 5, it's also clear that the introduction of a simple

alkoxy group could effectively tune the crystal structures. Herein, our original
expectation of achieving distinct diverse properties by a simple modification for the
bridging ligands of a series of gold complexes might be fulfilled successfully.

283 *3.4. AIE behaviors*

299

Based on the preceding mechanochromic investigation, we observed that all the 284 solid states for complexes 1–5 were luminescent, although their corresponding emission 285 intensities were not very remarkable. However, when we turned to explore their 286 corresponding solution states, we found that all the complexes were not luminescent, 287 which inspired us to associate with the AIE phenomenon. Therefore, using THF as a 288 good solvent and water as a poor solvent, we measured the UV-vis absorption spectra and 289 photoluminescence of complexes 1-5 in THF/H₂O mixtures with various water fractions 290 (f_w) . The corresponding data is listed in Table 2. As shown in Table 2, all the complexes 291 292 presented absorption peaks from 200-350 nm, which could be contributed to the π - π * transitions. On the other hand, the absorption evidently broadened and exhibited 293 distinctly various degree of red-shift when the water volumes were increased to a certain 294 value. At the same time, obvious level-off tails were also observed at long-wavelength 295 region, which might result from the presence of real nano-aggregates [46-47]. The 296 formation of aggregates was confirmed by DLS (Dynamic Light Scattering) study and the 297 related data have been showed in Figure S11. 298

Emission spectra demonstrated that their respective aggregation processes would be 300 lighted when the poor solvents were added to the solution. Complexes 1 (tert-butyl 301 substituted) and 2 (cyclohexyl substituted) exhibited typical AIE behavior, which 302 displayed continually increased luminescence during the aggregation process. Complex 1 303 presented one weak emission band with λ_{max} at around 375 nm in pure THF. However, 304 the original emission intensity decreased and a new broad peak at 500-600 nm appeared 305 exhibiting yellow emission when the water fraction was increased to 90%. The 306 corresponding emission intensity boosted markedly over 20-times compared with it being 307 in pure THF. A similar AIE phenomenon was observed for complex 2. The original weak 308 emission in pure THF solution was around 408 nm and further aggregation induced 309 emission appeared at around 557 nm, and equally raising f_w gave rise to dramatic increase 310 of the emission intensity over than 40-times. Actually, this is because that these 311 complexes are soluble in THF solution but practically immiscible with water. Raising 312 water contents will certainly reduce its dissolving capacity, which further results in the 313 generation of aggregated nanoparticles in THF/H₂O mixture with a high f_w value. On the 314 other hand, intermolecular distance containing gold-gold distances will be altered and 315 aurophilic interactions will form [48]. The above factors will ultimately lead to the 316 enhancement of emission intensity and the appearance of red-shifted yellow emission. 317 Distinctively, replacing the substituents from non-aromatic rings to phenyl or naphthyl 318 ring, the aggregation behaviors for complexes 3-5 are special but consistent. Complexes 319 **3-5** all began to emit when the f_w values were increased to 70% with new peaks at 419 320

nm (3), 627 nm (4), and 512 nm (5), respectively. Meanwhile, their respective emission 321 intensity reached the maximum, while their emission weakened gradually when the f_w 322 value was increased continuously to 80% and even 90%. Herein, we have to address a 323 question: what's the reason for the above subsequent quenching phenomenon. We 324 tentatively presume that further aggregations not only shortened the gold-gold distances, 325 but also tightened the intermolecular interactions between aromatic rings especially the 326 π - π interactions for complexes 4 and 5, which adversely lead to the quenching of the 327 initial luminescence. Actually, as collected in Table 2, the red-shifted absorptions after 328 aggregation might provide a support for our above presumption. 329

330

Insert Figure 7

331 **4.** Conclusion

In summary, five novel gold(I) complexes with various isocyanide ligands were 332 designed and synthesized. The elaborate modification of the terminal ligands has been 333 proved to effectively tune their photophysical properties. Alkyl modified complexes 1-3 334 exhibited tricolor or bicolor switching mechanochromic behaviors involved in a 335 reversible conversion between crystalline state and amorphous phase. Based on the 336 crystal analysis, the loosing packings formed through multiple intermolecular C-H···F 337 interactions might be the reason for the above mechanochromism. Conversely, the aryl 338 bridged complexes 4 and 5 are not mechano-responsive due to the tight and strong 339 intermolecular π - π packings. In addition, the structural difference of the terminal ligands 340

341	gives rise to distinctive AIE characteristics for complexes 1-5. The X-ray single-crystal
342	analysis of complex 2 also indicates that the equatorial $(e-)$ and axial $(a-)$ conformers
343	could stably coexist and could realize a lower-energy intermolecular charge transfer,
344	which is quite rare in the similar gold systems and could provide new information for
345	related molecule designing. The above prominent mechanochromic properties may
346	establish the foundation for their applications in mechanical sensors, and chemical
347	detectors. All the complexes present typical AIE characteristics and these AIE-gens are
348	hoped to be used in the field of biomedical imaging.
349	Acknowledgements
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351	Foundation of China (21472059, 21772054), and the 111 Project (B17019).
352	Supporting Information Available
353	Crystallographic data for the structures in this paper have been deposited with the
354	Cambridge Crystallographic Data Centre as supplemental publication CCDC 1564070
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511 Table of Contents

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- 515 tetrahydrothiophene.
- 516 3. **Table 1** Optical properties of complexes 1-5 in solid states.
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535



537 **Figure 1.** Molecule structure of complexes 1-5.



539 Scheme 1. Reagents and conditions: i) HCOOH, reflux; ii) Triphosgene, Et₃N, CH₂Cl₂;

540 iii) $C_{10}H_{21}Br$, K_2CO_3 , DMF; iv) Au(C_6F_5)(tht), CH₂Cl₂, tht = tetrahydrothiophene.

541	Table 1	Optical	properties	of com	plexes 1	- 3 in	different	solid s	tates.
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Complex		Solid states	
Complex	Unground powder	Ground powder	Treated with DCM
1	$465 \text{ nm}^{a}(3.7\%)^{b}$	495 nm (24.2%)	560 nm (3.5%)
2	466 nm (6.3%)	484 nm (10.9%)	466 nm
3	398, 416 nm (27.7%)	489 nm (61.3%)	398, 416 nm

542 ^aEmission maximum wavelength ($\lambda_{em,max}$). ^bAbsolute photoluminescence quantum yield.



Figure 2. (a) PL spectra ($\lambda_{ex} = 365$ nm) and (b) XRD patterns of complex 1 in different solid states. (c) Photographs of complex 1 in different situations taken under the 365 nm UV lamp.



547

- 548 Figure 3. Photographs of complexes 2(a) and 3(b) in different situations taken
- 549 under the 365 nm UV lamp.



551 Figure 4. (a) The single crystal structure of complex 2. (b) Intermolecular interactions

and (c) crystal packing diagram of complex 2.



Figure 5. (a) The single crystal structure of complex **4**. (b) Intermolecular interactions

and (c) crystal packing diagram of complex **4**.



Figure 6. The molecular orbitals and corresponding energies of monomer (*e*- and *a*-conformer) and dimer of complex **2**. The geometry optimizations are based on the crystal structures.

561	Table 2 (Optical p	properties	of comp	lexes 1-5	5 in s	solution	and aggregates.
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Commlex	Absorbance max	ximum (λ_{abs} , nm)	Emission maximum (λ_{em} , nm)		
Complex	Solution state	Aggregate state	Solution state	Aggregate state	
1	254	256		556	
2	255	257		557	
3	239	270		419	
4	306	336		627	
5	238,325	251,327		512, 551, 596	



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Figure 7. PL spectra (a) of the dilute solutions of complex **5** (20 μ M, $\lambda_{ex} = 325$ nm) in THF/H₂O mixtures with various water fractions (f_w). (b) Plot of relative emission peak intensity (I/I_0) at 512 nm versus f_w of the THF/water mixture, where I = emission intensity and $I_0 =$ emission intensity in THF solution. (c) Photos taken under 365 nm UV light of complex **5** in THF-water mixtures.

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572	Electronic Supplementary Information (ESI)
573	Different Structures Modulated Mechanochromism and
574	Aggregation-induced Emission in a series of Gold(I) Complexes
575	Xiao-Yan Wang ^{a,‡} , Jing Zhang ^{a,‡} , Yu-Bao Dong ^a , Yiyue Zhang ^a , Jun Yin ^{a,} *, Sheng Hua
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593 1. Crystallographic Details

Single crystals of complexes 1-5 were obtained by slow crystallization from 594 595 CH₂Cl₂/(MeOH or hexane), and approximate dimensions were showed in Table 1. They 596 were mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Ka radiation (0.71073 Å) at room 597 temperature. The structures were solved by a combination of direct methods 598 (SHELXS-97)¹ and Fourier difference techniques and refined by full-matrix least-squares 599 (SHELXL-97)². All non-H atoms were refined anisotropically. The H atoms were placed 600 in the ideal positions and refined as riding atoms. Further crystal data is provided in Table 601 S1. Bond distances and angles is given in Table S2. Crystallographic data for the 602 structures in this paper have been deposited with the Cambridge Crystallographic Data 603 Centre as supplemental publication CCDC 1564070 (1), 1564074 (2), 1564075 (3), 604 1564076 (4), 1564091(5). 605

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Complex	1	2	3	4	5
Formula	C ₁₁ H ₉ AuF ₅ N	C ₁₃ H ₁₁ AuF ₅ N	2(C ₁₅ H ₉ AuF ₅ N) , C ₂ H ₇ O	C ₁₇ H ₈ AuF ₅ N	C ₂₇ H ₂₆ AuF ₅ N O
Formula weight	447.16	473.19	1037.48	518.21	672.45
Temperature (K)	297(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	Imma	<i>P</i> -1	C2/c	C2/c	<i>P</i> -1
<i>a</i> (Å)	7.075(4)	11.053(4)	8.843(3)	8.337(4)	9.253(2)
$b(\text{\AA})$	10.387(7)	11.816(5)	29.114(9)	31.252(13)	9.283(2)
$c(\text{\AA})$	18.193(11)	12.210(5)	6.981(2)	6.881(3)	16.111(4)
α (°)	90	75.392(6)	90	90	86.783(3)
eta (°)	90	64.248(5)	111.964(4)	106.231(7)	81.267(4)
γ (°)	90	78.628(6)	90	90	71.397(3)
$V(\text{\AA}^3)$	1336.9(14)	1382.7(9)	1666.8(9)	1721.3(13)	1296.3(5)
Ζ	4	4	4	4	2
Density (calculated) (Mg/m ³)	2.401	2.273	2.067	2.000	1.723

Table S1. Crystal data and parameters of data collection and refinement for complexes 1–5.

Absorption coefficient (mm ⁻¹)	11.053	10.684	8.875	2.000	1.723
F(000)	896	880	974	964	654
Crystal size (mm ³)	0.20×0.12×0.1 2	0.10×0.10×0.1 0	0.10×0.10×0.1 0	0.12×0.10×0.1 0	0.15×0.12×0.1 0
Theta range for data collection (°)	2.24 to 23.79	1.79 to 25.01	1.4 to 28.38	3.35 to 25.08	1.28 to 26.00
Index ranges	-7≤h≤8, -11≤k≤11, -20≤l≤20	-12≤ <i>h</i> ≤13, -14≤ <i>k</i> ≤13, -14≤ <i>l</i> ≤14	-11≤ <i>h</i> ≤11, -37≤ <i>k</i> ≤38, -9≤ <i>l</i> ≤9	-9≤h≤9, -36≤k≤37, -7≤l≤8	-11≤h≤11, -11≤k≤11, -18≤l≤19
Reflections collected	3426	8474	7278	5927	9693
Independent reflections	611 [<i>R</i> (int) = 0.0806]	4787 [<i>R</i> (int) = 0.0748]	2080 [<i>R</i> (int) = 0.0462]	1520 [R(int) = 0.1383]	5059 [<i>R</i> (int) = 0.0449]
Max. and min. transmission	0.265 and 0.222	0.357 and 0.344	0.428 and 0.412	0.423 and 0.371	0.564 and 0.443
Data / restraints / parameters	611 / 59 / 73	4787 / 74 / 337	2080 / 13 / 124	1520 / 12 / 117	5059 / 0 / 317
Goodness-of-f it on F^2	1.093	1.054	1.084	1.084	1.056
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0932, wR2 = 0.2204	R1 = 0.1114, wR2 = 0.2817	R1 = 0.0331, wR2 = 0.0829	R1 = 0.0702, wR2 = 0.1733	R1 = 0.0604, wR2 = 0.1667
R indices (all data)	R1 = 0.1210, wR2 = 0.2414	R1 = 0.1542, wR2 = 0.3165	R1 = 0.0483, wR2 = 0.0946	R1 = 0.0928, wR2 = 0.1949	R1 = 0.0696, wR2 = 0.1805
Largest diff. peak and hole (e. ⁻³)	2.833 and -1.991	5.889 and -2.845	1.374 and -1.602	1.408 and -1.179	2.692 and -2.095

Table S2. Selected bond lengths (Å) and angles (deg) of complex 1.

Bond distances (Å)					
Au(1)-C(5)	1.99(3)	Au(1)-C(1)	2.07(6)		
C(1)-N(1)	1.09(6)	C(2)-N(1)	1.38(6)		
C(2)-C(3)	1.508(11)	C(2)-C(4)	1.510(11)		
C(3)-H(3A)	0.9600	C(3)-H(3B)	0.9600		
C(3)-H(3C)	0.9600	C(4)-H(4A)	0.9600		
C(4)-H(4B)	0.9600	C(4)-H(4C)	0.9600		
C(5)-C(6)	1.386(10)	C(5)-C(6)#1	1.386(10)		
C(6)-F(1)	1.384(10)	C(6)-C(7)	1.389(10)		
C(7)-C(8)	1.384(10)	C(7)-F(2)	1.386(10)		
C(8)-C(7)	1.384(10)	C(8)-F(3)	1.387(10)		
	Bond a	angles (°)			
C(5)-Au(1)-C(1)	180.0	N(1)-C(1)-Au(1)	180.0		
N(1)-C(2)-C(3)	106(3)	N(1)-C(2)-C(4)	100(6)		
C(3)-C(2)-C(4)	114.6(17)	C(2)-C(3)-H(3A)	109.5		
C(2)-C(3)-H(3C)	109.5	H(3A)-C(3)-H(3C)	109.5		
H(3B)-C(3)-H(3C)	109.5	C(2)-C(4)-H(4A)	108.8		

C(2)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.8	H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5	C(6)-C(5)-C(6)	118(2)
C(6)-C(5)-Au(1)	120.9(11)	F(1)-C(6)-C(5)	124.4(18))
F(1)-C(6)-C(7)	114.7(17)	C(5)-C(6)-C(7)	120.9(16)
C(8)-C(7)-F(2)	119.1(19)	C(8)-C(7)-C(6)	120.8(15)
F(2)-C(7)-C(6)	120.2(18)	C(7)-C(8)-C(7)	118(2)
C(7)-C(8)-F(3)	120.8(10)	C(1)-N(1)-C(2)	180.0(17)

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Table S3. Selected bond lengths (Å) and angles (deg) of complex 2.

Bond distances (Å)					
Au(1)-C(7)	1.92(2)	Au(1)-C(1)	2.041(11)		
Au(2)-C(20)	2.02(2)	Au(2)-C(14)	2.059(11)		
C(1)-C(2)	1.3900	C(1)-C(6)	1.3900		
C(2)-F(1)	1.238(19)	C(2)-C(3)	1.3900		
C(3)-F(2)	1.26(2)	C(3)-C(4)	1.3900		
C(4)-F(3)	1.337(18)	C(4)-C(5)	1.3900		
C(5)-F(4)	1.333(19)	C(5)-C(6)	1.3900		
C(6)-F(5)	1.38(2)	C(7)-N(1)	1.18(3)		
C(8)-N(1)	1.429(10)	C(8)-C(9)	1.512(10)		
C(8)-C(13)	1.513(10)	C(8)-H(8)	0.9800		
Bond angles (°)					

C(7)-Au(1)-C(1)	173.9(8)	C(20)-Au(2)-C(14)	176.5(8)
C(2)-C(1)-C(6)	120.0	C(2)-C(1)-Au(1)	119.8(9)
C(6)-C(1)-Au(1)	120.2(9)	F(1)-C(2)-C(1)	121.0(15)
F(1)-C(2)-C(3)	119.0(15)	C(1)-C(2)-C(3)	120.0
F(2)-C(3)-C(4)	118.6(16)	F(2)-C(3)-C(2)	121.3(16)
C(4)-C(3)-C(2)	120.0	F(3)-C(4)-C(5)	115.1(16)
F(3)-C(4)-C(3)	124.9(16)	C(5)-C(4)-C(3)	120.0
F(4)-C(5)-C(4)	115.7(16)	F(4)-C(5)-C(6)	124.3(16)
C(4)-C(5)-C(6)	120.0	F(5)-C(6)-C(5)	115.8(13)
F(5)-C(6)-C(1)	124.2(13)	C(5)-C(6)-C(1)	120.0

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Table S4. Selected bond lengths (Å) and angles (deg) of complex 3.

Bond distances (Å)					
Au(1)-C(1)	2.027(6)	C(6)-C(7)	1.398(7)		
Au(1)-C(5)	1.970(9)	C(6)-C(7A)	1.398(7)		
F(1)-C(2)	1.352(8)	C(7)-C(8)	1.378(8)		
F(2)-C(3)	1.345(9)	C(7)-C(10)	1.499(10)		
F(3)-C(4)	1.337(10)	C(8)-C(9)	1.376(9)		
O(1)-C(11)	1.41(4)	C(8)-H(8)	0.9300		
O(1)-O(1B)	1.18(5)	C(9)-H(9)	0.9300		
O(1)-H(1)	0.8200	C(10)-H(10C)	0.9600		
N(1)-C(5)	1.115(11)	C(10)-H(10A)	0.9600		

N(1)-C(6)	1.430(8)	C(10)-H(10B)	0.9600		
Bond angles (°)					
C(1)-Au(1)-C(5)	180.00(1)	C(6)-C(7)-C(10)	121.4(6)		
O(1B)-O(1)-H(1)	100.00	C(8)-C(7)-C(10)	121.4(6)		
C(5)-N(1)-C(6)	180.00(1)	C(6)-C(7)-C(8)	117.2(6)		
Au(1)-C(1)-C(2A)	122.9(3)	C(7)-C(8)-C(9)	121.4(7)		
C(2)-C(1)-C(2A)	114.2(5)	C(8)-C(9)-C(8A)	120.1(7)		
Au(1)-C(1)-C(2)	122.9(3)	C(9)-C(8)-H(8)	119.00		
F(1)-C(2)-C(3)	115.2(6)	C(7)-C(8)-H(8)	119.00		
C(1)-C(2)-C(3)	124.1(6)	C(8)-C(9)-H(9)	120.00		
F(1)-C(2)-C(1)	120.7(5)	C(8A)-C(9)-H(9)	120.00		
F(2)-C(3)-C(4)	119.5(6)	С(7)-С(10)-Н(10А)	110.00		

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 Table S5. Selected bond lengths (Å) and angles (deg) of complex 4.

Bond distances (Å)					
N(1)-C(14)	1.202(10)	N(1)-C(1)	1.414(10)		
N(1)-H(1)	0.5060	C(1)-C(2)	1.3900		
C(1)-C(6)	1.3693	C(1)-H(1)	0.9367		
C(2)-C(3)	1.3900	C(2)-H(2)	0.9300		
C(3)-C(4)	1.3900	C(3)-H(3)	0.9300		
C(4)-C(5)	1.4134	C(4)-H(4)	0.9300		
C(5)-C(6)	1.3890	C(5)-C(4)#1	1.418(19)		

C(6)-C(1)#1	1.367(14)	C(7)-C(8)	1.389(6)		
C(7)-C(8)#1	1.389(6)	C(7)-Au(1)#1	2.106(11)		
C(7)-Au(1)	2.106(11)	C(8)-F(1)	1.315(11)		
Bond angles (°)					
C(14)-N(1)-C(1)	161.5(17)	C(14)-N(1)-H(1)	151.4		
C(1)-N(1)-H(1)	15.7	C(2)-C(1)-C(6)	119.4		
C(2)-C(1)-N(1)	120.6(4)	C(6)-C(1)-N(1)	119.8(4)		
C(2)-C(1)-H(1)	123.0	C(6)-C(1)-H(1)	117.3		
N(1)-C(1)-H(1)	8.4	C(1)-C(2)-C(3)	120.0		
C(1)-C(2)-H(2)	120.0	C(3)-C(2)-H(2)	120.0		
C(4)-C(3)-C(2)	120.0	C(4)-C(3)-H(3)	120.0		
C(2)-C(3)-H(3)	120.0	C(3)-C(4)-C(5)	120.5		
C(3)-C(4)-H(4)	119.7	C(5)-C(4)-H(4)	119.7		
C(4)-C(5)-C(6)	117.4	C(4)-C(5)-C(4)#1	125.7(4)		

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Table S6. Selected bond lengths (Å) and angles (deg) of complex 5.

Bond distances (Å)							
	Au(1)-C(7)	1.957(10)	Au(1)-C(1)	2.014(8)			
	C(1)-C(2)	1.366(11)	C(1)-C(6)	1.399(12)			
	C(2)-F(1)	1.339(9)	C(2)-C(3)	1.396(13)			
	C(3)-F(2)	1.347(11)	C(3)-C(4)	1.367(14)			
	C(4)-F(3)	1.333(11)	C(4)-C(5)	1.368(15)			

C(5)-C(6)	1.340(15)	C(5)-F(4)	1.357(11)			
C(6)-F(5)	1.351(10)	C(7)-N(1)	1.155(12)			
C(8)-C(9)	1.374(12)	C(8)-C(17)	1.398(11)			
C(8)-N(1)	1.404(12)	C(9)-C(10)	1.375(13)			
C(9)-H(9)	0.9300	C(10)-C(11)	1.375(11)			
Bond angles (°)						
C(7)-Au(1)-C(1)	179.7(3)	C(2)-C(1)-C(6)	114.3(8)			
C(2)-C(1)-Au(1)	122.1(6)	C(6)-C(1)-Au(1)	123.6(6)			
F(1)-C(2)-C(1)	120.7(8)	F(1)-C(2)-C(3)	116.2(7)			
C(1)-C(2)-C(3)	123.1(8)	F(2)-C(3)-C(4)	119.7(9)			
F(2)-C(3)-C(2)	121.0(9)	C(4)-C(3)-C(2)	119.3(8)			
F(3)-C(4)-C(3)	119.5(9)	F(3)-C(4)-C(5)	121.4(10)			
C(3)-C(4)-C(5)	119.1(9)	C(6)-C(5)-F(4)	122.1(10)			
C(6)-C(5)-C(4)	120.1(8)	F(4)-C(5)-C(4)	117.7(10)			
C(5)-C(6)-F(5)	117.3(8)	C(5)-C(6)-C(1)	124.1(8)			
F(5)-C(6)-C(1)	118.6(8)	N(1)-C(7)-Au(1)	178.1(8)			
X /						



630

Figure S1. (a) The single crystal structure of complex **1**. (b, c) Intermolecular interactions and (d,

e) crystal packing diagram of complex **1**.





and (d, e) crystal packing diagram of complex **3**.



639 Figure S3. (a) The single crystal structure of complex 5. (b, c) Intermolecular interactions and



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Figure S4. (a) PL spectra ($\lambda_{ex} = 365$ nm) and (b) XRD patterns of complex **2** in different solid

644 states.



646 Figure S5. (a) PL spectra ($\lambda_{ex} = 365$ nm) and (b) XRD patterns of complex 3 in different solid 647 states.

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Figure S6. Absorption of the dilute solutions of complex **5** (20 μ M) in THF/H₂O mixtures with

651 various water fractions ($f_{\rm w}$).



Figure S7. Absorption (a) and PL spectra (b) of the dilute solutions of complex **1** (20 μ M, λ_{ex} = 365 nm) in THF/H₂O mixtures with various water fractions (f_w), excitation wavelength: 365 nm. (c) Changes in emission intensity of **1** at 556 nm in THF/H₂O mixtures with different water contents. (d) Photographs are the fluorescence images of complex **1** with f_w value from 0% to 90%.



Figure S8. Absorption (a) and PL spectra (b) of the dilute solutions of complex **2** (20 μ M, λ_{ex} = 365 nm) in THF/H₂O mixtures with various water fractions (f_w), excitation wavelength: 365 nm. (c) Changes in emission intensity of complex **2** at 557 nm in THF/H₂O mixtures with different water contents. (d) Photographs are the fluorescence images of complex **2** with f_w value from 0% to 90%.



Figure S9. Absorption (a) and PL spectra (b) of the dilute solutions of complex **3** (20 μ M, λ_{ex} = 365 nm) in THF/H₂O mixtures with various water fractions (f_w), excitation wavelength: 365 nm. (c) Changes in emission intensity of **3** at 556 nm in THF/H₂O mixtures with different water contents. (d) Photographs are the fluorescence images of complex **3** with f_w value from 0% to 90%.

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Figure S10. Absorption (a) and PL spectra (b) of the dilute solutions of complex 4 (20 μ M, λ_{ex} = 365 nm) in THF/H₂O mixtures with various water fractions (f_w), excitation wavelength: 365 nm. (c) Changes in emission intensity of 4 at 556 nm in THF/H₂O mixtures with different water contents. (d) Photographs are the fluorescence images of complex 4 with f_w value from 0% to 90%.

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Figure S11. Average particle size distribution of complexes 1-5 at different water volume fractions (f_w) in THF/H₂O.

689 NMR spectra













¹H NMR in DMSO-*d*₆, 600 MHz





8.14 8.14 8.12 8.12 8.09 7.7.39 7.7.81 7.7.72 7.7.73 7.7.72 7.7.73 7.7.75 7.7.75 7.7.75 7.7.75 7.7.55 7.7.55 7.7.55

¹H NMR in CDCl₃, 400 MHz













Highlights

- Five novel gold(I) complexes with various isocyanide ligands have been synthesized and characterized.
- Alkyl modified Au(I) complexes exhibit infrequent tricolor or reversible bicolor mechanochromic behaviors.
- All the target complexes present prominent but different aggregation-induced emission(AIE) characteristics.
- The equatorial (e-) and axial (a-) conformers could stably coexist in the same unit cell for cyclohexyl isocyanide gold(I) complex, which is quite rare in the similar gold systems.