Dyes and Pigments 95 (2012) 485–490

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis, characterization and mechanochromic behavior of binuclear gold (I) complexes with various diisocyano bridges

Jinhua Liang, Fang Hu, Xiaoyi Lv, Zhao Chen, Zhiming Chen, Jun Yin*, Guang-Ao Yu, Sheng Hua Liu*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

ARTICLE INFO

Article history:
Received 17 May 2012
Received in revised form
21 June 2012
Accepted 22 June 2012
Available online 29 June 2012

Keywords:
Crystal structure
Mechanochromism
Gold (I) complexe
Stimuli-responsive luminescence
Diisocyano bridges
Effects of structure

ABSTRACT

A series of binuclear gold (I) complexes were synthesized. Their structures were characterized by elemental analyses, IR spectrometry, UV–Vis spectroscopy and single crystal X-ray diffraction. Their fluorescent mechanochromic (tribochromic) properties were investigated. The results of the mechanochromic studies suggested that the gold complexes with methylsubstituted phenyl bridges exhibited mechanochromism and a 100 nm red-shift of fluorescent spectrum could be observed after grinding. The complex with a diphenylmethane bridge exhibited mechanochromism with a change in fluorescence from green to blue (25 nm red-shift after grinding). The ground complexes reverted to their original states by treatment with CH_2Cl_2. No mechanochromism was observed for either the biphenyl or diphenylethane containing complexes.

1. Introduction

Color chemistry is attracting significant attention as a consequence its wide applications in colorimetric probes, fluorescent imaging and modern dyes. Color change is very important for many applications [1]. In solution, the introduction of other species may affect and change the color of compounds possibly owing to electron or energy transfer. Additionally, the self-assembling style of the molecule is also very important factor to change the color of the compound [2,3]. Temperature, density and solvent of the system can effectively adjust the molecular configuration. While the molecular packing is generally steady when the compound is in the solid state. Conveniently changing the color of the compound in the solid will remains a challenging project [4–7].

Mechanochromism is an overarching term that describes the phenomenon of color change caused by mechanical grinding, crushing or rubbing which is also known as tribochromism [8] or pressing, also termed piezochromism [8], of the solid sample and reversion to the original color by, for example, heating or recrystallization. Some studies on organic chromophores [9–20] and dye-doped polymers [21–28] showed that absorption or emission spectra could be changed by grinding [29]. In comparison with packing changes of organic compounds, metal complexes can utilize metal–metal interaction to adjust their optoelectronic properties. Several examples of multinuclear organometallic complexes have been reported, and the results indicated that some changes on the absorption and emission could be observed after grinding [30–45]. As early as 2002, Catalano and Horner have reported that the colorless, binuclear gold (I) complex $[Au_2(dpim)_2](ClO_4)_2 \cdot 2$ MeCN (dpim = 2-(diphenylphosphanyl)-1-methylimidazole) exhibited an orange emission, however, the material showed a stronger blue emission after grinding [34]. Recently, the gold (I) complex $[(C_6F_5Au)_2(\mu$-1,4-diisocyanobenzene)] based on isocyano ligand displayed from blue to yellow mechanochromic behavior reported by Ito et al, owing to closed-shell aurophilic interactions [31]. In view of this isocyano gold (I) complex, we only had a rudimentary understanding of the relationship between structure and mechanochromic activity. Herein, we designed and synthesized a series of diisocyano-based gold (I) complexes, and confirmed their structures, and investigated the effect of ligand structures towards mechanochromic activity.

2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise

---

* Corresponding authors. Tel./fax: +86 27 67867725.
E-mail addresses: yinj@mail.ccnu.edu.cn (J. Yin), chshliu@mail.ccnu.edu.cn (S.H. Liu).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2012.06.014

stated. The starting materials $C_6F_5Au(tht)$ (tht = thiophane) [46] and middle isocyano bridge 1,4-diisocyano-2,5-dimethylbenzene (**3a**) [25], 1,4-diisocyano-2,3,5,6-tetramethylbenzene (**3b**) [47], 4,4′-diisocyanodiphenylmethane (**3c**) [48], 4,4′-biphenyldiisocyanide (**3d**) [48], 4,4′-(Ethane-1,2-diyl)dianiline (**1e**) [49] were prepared by procedures described in the literature. All other chemicals were obtained from commercial sources without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were collected on a Varian MERCURY Plus 400 spectrometer (400 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. UV–Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer. XRD studies were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite-monochromated Cu Kα radiation ($\lambda = 1.54$ Å, 40 kV, 30 mA).

2.2. Synthesis

2.2.1. Synthesis of diformamide ligand 2e

4,4′-(ethane-1,2-diyl)dianiline (4.7 mmol, 1.0 g) was dissolved in HCOOH (10 mL) and the mixture was heated under reflux for 12 h. After removal of the solvent, ethane (20 mL) was added to get a pale solid, which was collected by filtration, and washed with ethane and dried under vacuum. Yield: 0.78 g, 62%. ^1H NMR (400 MHz, d^6-DMSO): δ 2.80 (s, 4H, CH_2), 7.14 (d, $J = 7.2$ Hz, 4H, Ar–H), 7.48 (d, $J = 7.6$ Hz, 4H, Ar–H), 8.25 (s, 1 H, CHO_{cis}), 8.72 (d, $J = 10.8$ Hz, 1 H, CHO_{trans}), 10.04 (s, 1 H, NH_{trans}), 10.09 (br s, 1 H, NH_{cis}). ^{13}C NMR (100.6 MHz, d-DMSO): δ 36.53 (s, CH_2), 119.13, 128.76, 136.13, 136.75 (s, Ar), 159.43 (CHO). Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.65; H, 5.16; N, 11.95.

2.2.2. Synthesis of diisocyano ligand 3e

A dichloromethane solution (5 mL) of triphosgene (816 mg, 2.75 mmol) was added dropwise to dichloromethane solution (15 mL) of **2e** (670 mg, 2.5 mmol) and triethylamine (3.2 mL, 22.5 mmol) at 0 °C. After refluxing for 3 h, 10% aq. K_2CO_3 (50 mL) was added dropwise at room temperature. The mixture was extracted several times with CH_2C1_2. The combined organic phase was washed with water, dried over magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/CH_2C1_2 = 1:1) to give a white solid. Yield: 0.23 g, 40%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.93 (s, 4H, CH_2), 7.12 (d, $J = 8.4$ Hz, 4H, Ar–H), 7.28 (d, $J = 8.4$ Hz, 4H, Ar–H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 37.01 (s, CH_2), 126.37, 129.40, 142.39, 163.54 (s, Ar). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.49; H, 5.95; N, 10.36.

2.2.3. Synthesis of diisocyano-based complexes 4a–4e

General method: A mixture of $C_6F_5Au(tht)$ (0.52 mmol) and **3** (0.25 mmol) were stirred in CH_2Cl_2 (27 mL) for over night under an argon atmosphere at room temperature. The emerging precipitate was filtered, and washed with CH_2Cl_2, and dried in vacuo to obtain **4.** The NMR data of these compounds were not obtained due to the poor solubility.

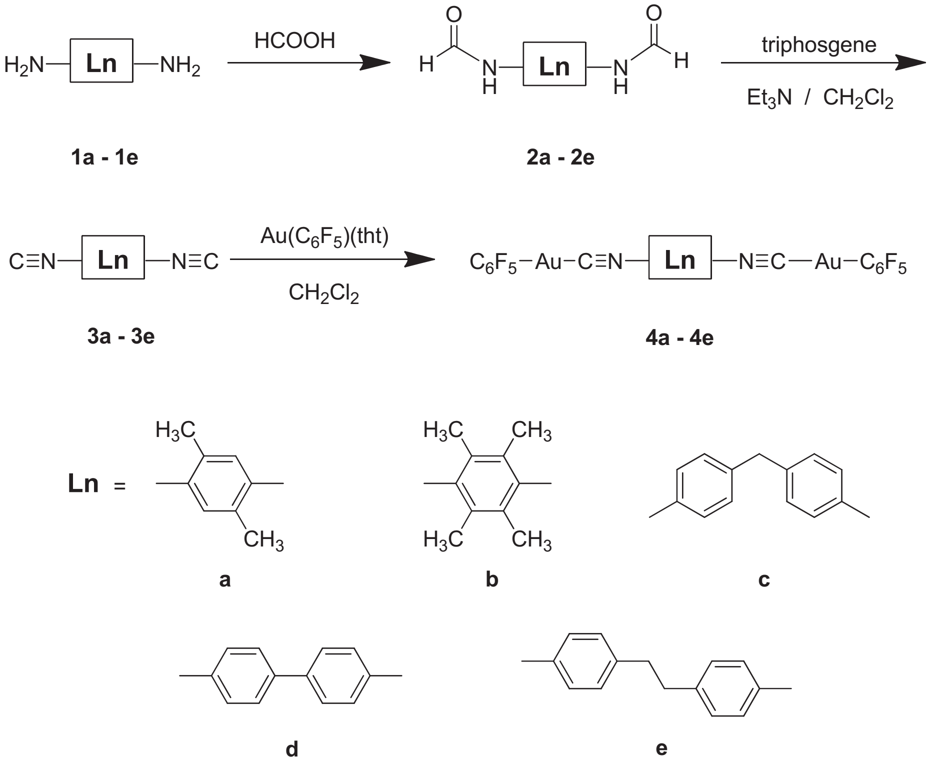
Compound **4a**: White solid, yield: 126 mg, 57%. Anal. Calcd for $C_{22}H_8Au_2F_{10}N_2$: C, 29.88; H, 0.91; N, 3.17. Found: C, 29.62; H, 0.95; N, 2.91. IR (KBr, ν in cm^{-1}): 2205 (N≡C).

Compound **4b**: White solid, yield: 157 mg, 69%. Anal. Calcd for $C_{24}H_{12}Au_2F_{10}N_2$: C, 31.60; H, 1.33; N, 3.07. Found: C, 31.42; H, 1.19; N, 2.91. IR (KBr, ν in cm^{-1}): 2209 (N≡C).

Compound **4c**: White solid, yield: 203 mg, 86%. Anal. Calcd for $C_{27}H_{10}Au_2F_{10}N_2$: C, 34.27; H, 1.07; N, 2.96. Found: 34.13; H, 0.95; N, 2.87. IR (KBr, ν in cm^{-1}): 2214 (N≡C).

Compound **4d**: White solid, yield: 184 mg, 79%. Anal. Calcd for $C_{26}H_8Au_2F_{10}N_2$: C, 33.50; H, 0.86; N, 3.00. Found: C, 33.56; H, 0.85; N, 2.96. IR (KBr, ν in cm^{-1}): 2220 (N≡C).

Compound **4e**: White solid, yield: 180 mg, 75%. Anal. Calcd for $C_{28}H_{12}Au_2F_{10}N_2$: C, 35.02; H, 1.26; N, 2.92 Found: C, 34.88; H, 1,18; N, 2.85. IR (KBr, ν in cm^{-1}): 2222 (N≡C).



Scheme 1. Synthesis of diisocyano-based binuclear gold (I) **4a**–**4e**.

3. Results and discussion

3.1. Discussion of the synthetic stragegy

The diisocyano-based binuclear gold (I) complexes **4a**–**4e** were synthesized according to Scheme 1. The intermediates **3a**–**3e** as starting materials were reacted with C_6F_5Au(tht) to afford the binuclear gold complexes **4a**–**4e** in good yields, respectively.

3.2. X-ray structures

3.2.1. Crystallographic details

The single crystals of complexes **4a, 4c** and **4e** suitable for X-ray analysis were obtained by recrystallization from chlorobenzene. The crystal of **4a, 4c** and **4e** were mounted on a glass fiber for the diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97) [50] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97) [51]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table 1. Selected bond distances and angles were given in Tables S1, S2 and S3 (Table 2).

3.2.2. X-ray structures of 4a, 4c and 4e

As shown in Fig. 1, the complex **4a** displayed completely symmetrical configuration. From the data in the supporting information, the bond length of C(39)–N(1) was 1.13 Å, which suggested that this carbon-nitrogen bond was a triple bond. According to the angle (176.2°) of C(39)–Au(1)–C(33), the compound was not linear. The packing of molecules presented a head-to-head arrangement pattern, as can be observed in Fig. S13. According to previous literature, it has been accepted that for such molecules intermolecular gold–gold interactions occur when the intermolecular distance between the gold atoms was within the range of 2.7–3.3 Å [52]. In this case, the distance of intermolecular gold atoms was 5.64 Å, indicating no obvious intermolecular gold–gold interaction. However, the existence of intermolecular C–H…F ($d_{H\ldots F}$ = 2.46 Å, 2.58 Å) and C–F (d_{C-F} = 3.05 Å, 3.14 Å) interactions promoted the molecular packing.

Table 1
Crystal data and refinement parameter of **4a, 4c** and **4e**.

	4a	4c	4e
Formula	C3.67, H1.33, Au0.33, F1.67 N0.33	C27, H10, Au2, F10, N2	C14, H6, Au, F5, N
Fw	147.37	946.30	480.16
Temp(K)	292(2)	292(2)	273(2)
Cryst syst	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	P2(1)/n
a (Å)	5.6470(7)	13.2394(14)	4.564(3)
b (Å)	10.1212(12)	19.366(2)	11.342(8)
c (Å)	10.8615(13)	10.2106(11)	25.478(16)
α(deg)	113.515(2)	90	90
β(deg)	93.893(2)	98.103(2)	90.369(10)
γ(deg)	99.398(2)	90	90
V (Å^{-3})	555.48(12)	2591.8(5)	1318.7(15)
Z	6	4	4
D_{calcd} (Mg cm^{-3})	2.643	2.425	2.418
Cryst size (mm^3)	0.16 × 0.15 × 0.12	0.16 × 0.12 × 0.10	0.2 × 0.2 × 0.2
F(000)	402	1736	884
Diffractometer	KappaCCD	KappaCCD	KappaCCD
Radiation	Mo K*a*	Mo K*a*	Mo K*a*
abs coeff (mm^{-1})	13.288	11.401	11.205
θ range (deg)	2.07 to 26.99	1.55 to 28.00	0.80 to 23.85
hkl range	−7 to 7, −12 to 12 −13 to 12	−17 to 17, −25 to 23 −13 to 13	−5 to 5 −12 to 12 −28 to 28
Reflections collected	4121	22944	7986
Independent reflections[R$_{(int)}$]	2383 (0.0269)	6234 (0.0389)	2006 (0.0836)
Data / restraints / parameters	2383/0/164	6234/0/371	2006/108/167
Final *R*	0.0378	0.0323	0.0761
R_w	0.1166	0.0805	0.1517
R (all date)	0.0469	0.0580	0.0886
R_w (all date)	0.1590	0.0885	0.1563
Goodness of fit/F^2	1.221	0.992	1.166
Largest diff peak, hole (e Å^{-3})	2.144 and −1.998	1.673 and −1.014	2.718 and −2.887

Table 2
Solid-State absorption and luminescence data of complexes **4a**–**4e** at ambient temperature.

Compound	λ_{abs}/nm	λ_{em}/nm	
		Before grinding	After grinding
4a	335	432, 459	531
4b	332	435, 469	528
4c	374	477	502
4e	332	405	405
4f	330	488	488

Because of the difference of structure compared to the structure of **4a**, the single crystal structure of structure **4c** compared the herring-bone shape in Fig. 2 and Fig. S14. And the two benzene rings were twisted and the dihedral angle was 82.9°, which was attributed to the insertion of the methylene unit. In this structure, the angles of C(16)–Au(1)–C(1) and C(15)–Au(2)–C(22) displayed similar angles (178.2 and 172.5°) with complex **4a**. Furthermore, the bond lengths of N(1)–C(1) and N(2)–C(15) were 1.132(7) Å and 1.147(8) Å corresponding to the carbon-nitrogen triple bond, which was in good agreement with complex **4a**. The molecular packing, depicted in Fig. S14, was arranged in a head-to-tail style and the distance of gold atoms was 3.23 Å, which clearly indicated intermolecular gold–gold interaction. Similarly the existence of weak intermolecular interactions (such as the C–H…F and C–F interactions). On the basis of **4c**, further insertion of the methylene group, viz. **4e**, made the molecule more linear than complex **4c**. The single crystal structure of **4e** is shown in Fig. 3. The bond lengths of the carbon-nitrogen triple bonds were similar to the complexes **4a** and **4c** as described in supporting information. While the distance of intermolecular gold atoms was 4.56 Å. Similar intermolecular C–H…F and C–F interactions could be observed. (Fig. S15).

3.3. Mechanochromism (tribochromism)

Subsequently, the mechanochromic properties of **4a**–**4e** were investigated. Firstly, we investigated their UV/Vis absorption spectra before and after grinding. The results suggested that no obvious changes were observed (In supporting information: Figs. S4–S8).

The emission spectra of **4a** [$(C_6F_5Au)_2$(μ-1,4-diisocyano-2,5-dimethylbenzene)] in various states were shown in Fig. 4. The emission spectra of the unground sample of **4a** displayed two emission bands at 432 nm and 460 nm, which could be attributed to the phosphorescence of the intraligand-localized π–π^* excited state [53]. After grinding of the sample, a broad emission band with a maximum wavelength at 530 nm was observed, in which aurophilic interactions may be responsible for the new ligand-to-metal charge transfer (LMCT) excited state [54]. Treatment of ground **4a** with dichloromethane induced reversion to the original state. Photographic images of the color and luminescence changes for **4a**

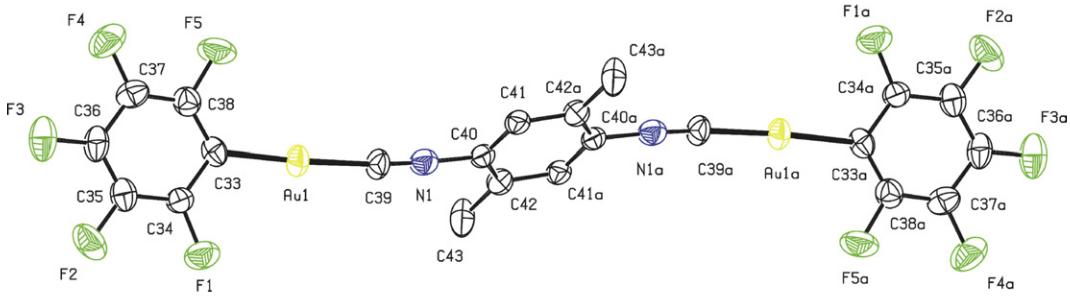


Fig. 1. The single crystal structure **4a**.

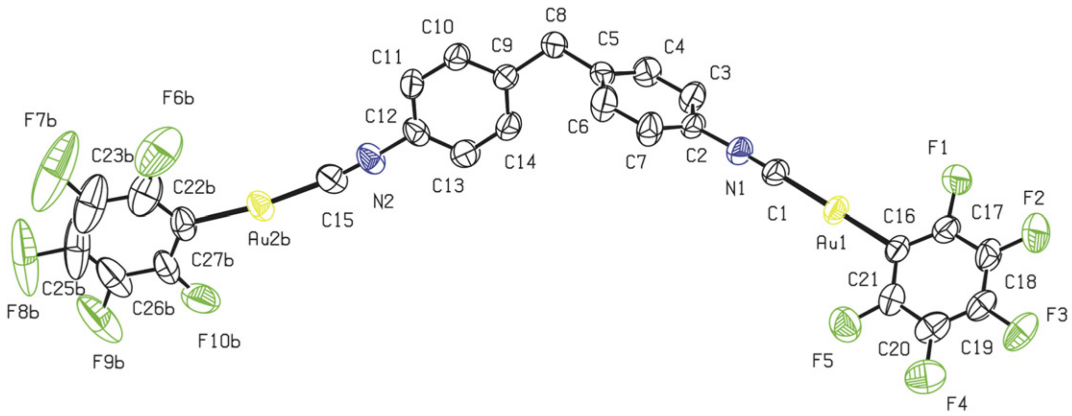


Fig. 2. The single crystal structure **4c**.

were presented in Fig. 4. The mechanochromic luminescence behavior of compound **4b** was similar to that of **4a** (Fig. S1). These results showed that the mechanochromic luminescence behavior of **4a** and **4b** were similar to that of [$(C_6F_5Au)_2(\mu$-1,4-diisocyanobenzene)] reported by Ito et al. [31]. Therefore, the introduction of methyl groups would not affect the mechanochromic behavior of the molecules. When dimethylbenzene in the bridge of **4a** was replaced for diphenylmethane to afford **4c**, the compound was also mechanochromically active. The emission spectra of compound **4c** in various states were indicated in Fig. 5. It showed a broad emission band with a maximum wavelength at 477 nm. After grinding, the maximum wavelength was red-shifted to 503 nm, following the blue-to-green emission process. Reversion to the original blue emission by treating the ground sample with dichloromethane was noted. Photographic images of the color and luminescence changes of **4c** were presented in Fig. 5, demonstrating its mechanochromic luminescence behavior. Although the methylene group was introduced to the molecule of complex **4c**, the molecular configuration remained stable. So complex **4c** possessed mechanochromic properties.

However, the emission spectra of **4d** containing two ethylene units between the terminal phenyl rings did not display any changes after grinding in an agate mortar (Fig. S2). For complex **4e**, the fluorescence spectra showed a broad emission band with a maximum wavelength at 404 nm (Fig. S3) and displayed a purple color. It was found that compound **4e**, like **4d**, did not exhibit any mechanochromic properties upon grinding. It was possible that the grinding did not lead to the difference of molecular packing and no obvious intermolecular gold–gold interactions were observed.

Additionally, X-ray powder diffractometry was used to further study the mechanochromic behavior. As presented in Fig. 6, the unground sample **4a** showed clear reflection peaks. In contrast, the XRD pattern of the ground sample showed significant changes, which indicated that the grinding caused a crystalline-to-metastable phase conversion. Upon treatment of the ground sample with dichloromethane, the reflection peaks were restored and corresponded to the original crystalline phase. The variations of the XRD patterns of **4b** and **4c** (Figs. S9 and S10) were similar to that of **4a**. While the non-mechanochromic species **4d** and **4e** were thoroughly ground, XRD patterns were essentially unchanged

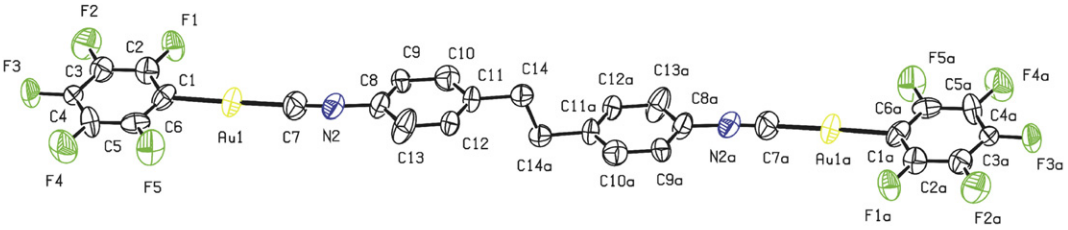


Fig. 3. The single crystal structure **4e**.

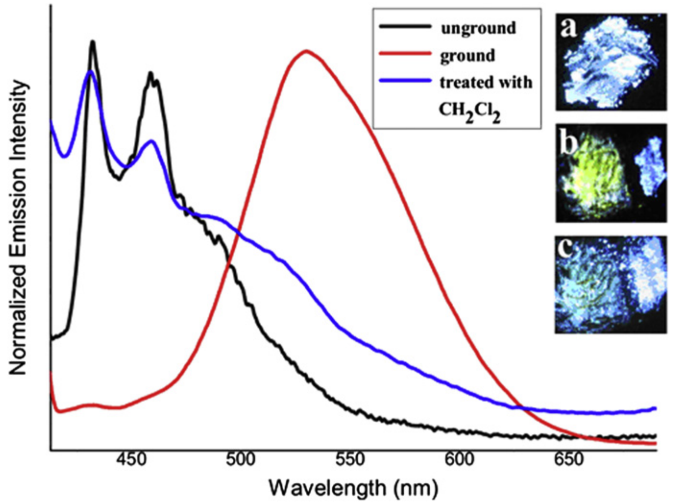


Fig. 4. Emission spectra of **4a** in various states. Insets show the fluorescence images of Au (I) complex **4a** powder under 365 nm UV light: a) before grinding, b) after grinding, c) after treatment with dichloromethane.

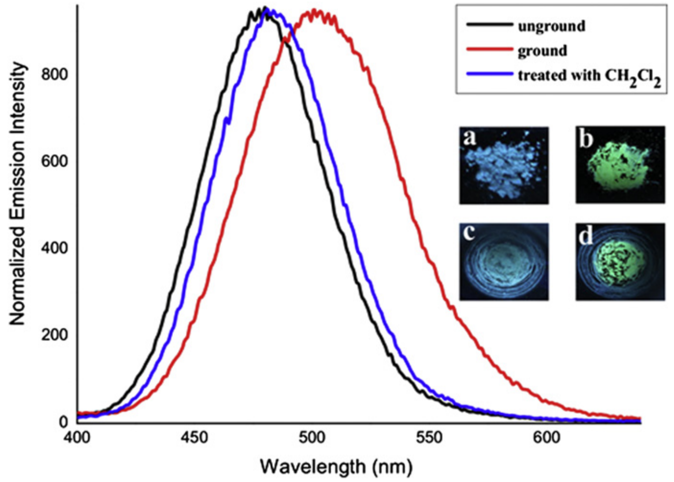


Fig. 5. Emission spectra of **4c** in various states. Insets show the fluorescence images of Au (I) complex **4c** powder under 365 nm UV light: a) before grinding, b) after grinding, c) after treatment with dichloromethane and d) repetition of the green yellow emission by scratching the powder with a pestle at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

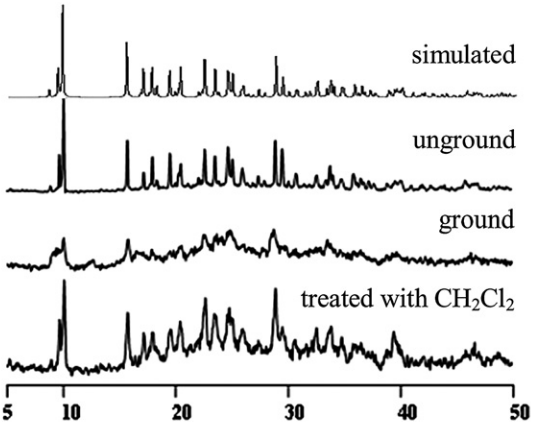


Fig. 6. XRD spectra of **4a** in various states.

(Figs. S11 and S12), which implied that no changes from crystalline to non-crystalline transition took place. According to above experiments, we concluded that (1) **4a** and **4b** with methyl-substituted phenyl bridges revealed mechanochromic properties, and a 100 nm red-shift of fluorescent spectrum could be observed after grinding; (2) the complex **4c** exhibited mechanochromic property and fluorescent change from green to blue fluorescence (25 nm red-shift after grinding); (3) the ground complexes **4a**, **4b** and **4c** could revert to the original states by treatment of the **4a, 4b** and **4c** with CH_2Cl_2; (4) no obvious color changes were observed when the complexes **4d** and **4e** were ground.

4. Conclusions

In this work, we reported a series of new binuclear gold (I) complexes with various diisocyano bridges and characterized their structures. Their mechanochromic properties indicated that the structure of ligand has a large effect on mechanochomic activity. In which, the binuclear gold (I) complexes **4a, 4b** and **4c** showed mechanochromic behavior, but **4d** and **4e** were mechanochromically inactive. In addition, our studies described the relationship of structure with mechanochromic activity. Therefore, further studies will focus on the functionalization of structures in order to find mechanochromic materials with excellent properties in the future.

Acknowledgments

The authors acknowledge financial support from National Natural Science Foundation of China (Nos. 20931006, 21072070, 21072071), Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0953), and the Program for Academic Leader in Wuhan Municipality (No. 201271130441), and self-determined research funds of CCNU from the colleges' basic research and operation of MOE.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.dyepig.2012.06.014.

References

[1] Zollinger H. Color chemistry: synthesis, properties and applications of organic dyes and pigments. New York: VCH; 1991.
[2] Kato T. Self-assembly of phase-segregated liquid crystal structures. Science 2002;295:2414–8.
[3] Kato T, Mizoshita N, Kishimoto K. Functional liquid-crystalline assemblies: self-organized soft materials. Angew Chem Int Ed 2005;45:38–68.
[4] Balch AL. Dynamische Kristalle: visuell wahrnehmbare mechanochemische lumineszenzänderungen von gold- und anderen Übergangsmetallkomplexen. Angew Chem 2009;121:2679–82.
[5] Balch AL. Dynamic crystals: visually detected mechanochemical changes in the luminescence of gold and other transition-metal complexes. Angew Chem Int Ed 2009;48:2641–4.
[6] Sagara Y, Kato T. Mechanically induced luminescence changes in molecular assemblies. Nat Chem 2009;1:605–10.
[7] Kaupp G. Mechanochemistry: the varied applications of mechanical bond-breaking. CrystEngComm 2009;11:388–403.
[8] Bamsfield P. Chromic phenomena: technological applications of color chemistry. Cambridge: RSC Publishing; 2001. p. 69.
[9] Chi Z, Zhang X, Xu B, Zhou X, Ma C, Zhang Y, et al. Recent advances in organic mechanofluorochromic materials. Chem Soc Rev 2012;41:3878–96.
[10] Sagara Y, Mutai T, Yoshikawa I, Araki K. Material design for piezochromic luminescence: hydrogen-bond-directed assemblies of a pyrene derivative. J Am Chem Soc 2007;129:1520–1.
[11] Zhang Z, Yao D, Zhou T, Zhang H, Wang Y. Reversible piezo- and photochromic behaviors accompanied by emission color switching of two anthracene-containing organic molecules. Chem Commun 2011;47:7782–4.

[12] Sagara Y, Kato T. Stimuli-responsive luminescent liquid crystals: change of photoluminescent colors triggered by a shear-induced phase transition. Angew Chem Int Ed 2008;47:5175–8.

[13] Teng MJ, Jia XR, Chen XF, Ma ZY, Jia XR. Mechanochromic luminescent property of a polypeptide-based dendron. Chem Commun 2011;47: 6078–80.

[14] Yoon SJ, Chung JW, Gierschner J, Kim KS, Choi MG, Kim D, et al. Multistimuli two-color luminescence switching via different slip-stacking of highly fluorescent molecular sheets. J Am Chem Soc 2010;132:13675–83.

[15] Ooyama Y, Kagawa Y, Fukuoka H, Ito G, Harima Y. Mechanofluorochromism of a series of benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes. Eur J Org Chem 2009;31:5321–6.

[16] Luo X, Li J, Li C, Heng L, Dong YQ, Liu Z, et al. Reversible switching of the emission of diphenyldibenzofulvenes by thermal and mechanical stimuli. Adv Mater 2011;23:3261–5.

[17] Li H, Zhang X, Chi Z, Xu B, Zhou W, Liu S, et al. New thermally stable piezofluorochromic aggregation-induced emission compounds. Org Lett 2011;13: 556–9.

[18] Dou C, Han L, Zhao S, Zhang H, Wang Y. Multi-stimuli-responsive fluorescence switching of a donor-acceptor π-conjugated compound. J Phys Chem Lett 2011;2:666–70.

[19] Zhang X, Chi Z, Zhang J, Li H, Xu B, Li X, et al. Piezofluorochromic properties and mechanism of an aggregation-induced emission enhancement compound containing N-hexyl-phenothiazine and anthracene moieties. J Phys Chem B 2011;115:7606–11.

[20] Kunzelman J, Kinami M, Crenshaw BR, Protasiewicz JD, Weder C. Oligo(p-phenylene vinylene)s as a “new” class of piezochromic fluorophores. Adv Mater 2008;20:119–22.

[21] Davis DA, Hamilton A, Yang J, Cremar LD, van Gough D, Potisek SL, et al. Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. Nature 2009;459:68–72.

[22] Pucci A, Ruggeri G. Mechanochromic polymer blends. J Mater Chem 2011;21: 8282–91.

[23] Caruso MM, Davis DA, Shen Q, Odom SA, Sottos NR, White SR, et al. Mechanically-induced chemical changes in polymeric materials. Chem Rev 2009;109:5755–98.

[24] Ariga K, Mori T, Hill JP. Mechanical control of nanomaterials and nanosystems. Adv Mater 2012;24:158–76.

[25] O’Bryan G, Wong BM, McElhanon JR. Stress sensing in polycaprolactone films via an embedded photochromic compound. ACS Appl Mater Interfaces 2010; 2:1594–660.

[26] Lee CK, Davis DA, White SR, Braun PV. Force-induced redistribution of a chemical equilibrium. J Am Chem Soc 2010;132:16107–11.

[27] Crenshaw BR, Weder C. Deformation-induced color changes in melt-processed photoluminescent polymer blends. Chem Mater 2003;15:4717–24.

[28] Duan LL, You B, Wu LM, Chen M. Facile fabrication of mechanochromic-responsive colloidal crystal films. J Colloid Interface Sci 2011;353:163–8.

[29] Beyer MK, Clausen-Schaumann H. Mechanochemistry: The mechanical activation of covalent bonds. Chem Rev 2005;105:2921–48.

[30] Laguna A, Lasanta T, López-de-Luzuriaga JM, Monge M, Naumov P, Olmos ME. Combining aurophilic interactions and halogen bonding to control the luminescence from bimetallic gold-silver clusters. J Am Chem Soc 2010;132: 456–7.

[31] Ito H, Saito T, Oshima N, Kitamura N, Ishizaka S, Hinatsu Y, et al. Reversible mechanochromic luminescence of $[(C_6F_5Au)_2(\mu$-1,4-Diisocyanobenzene)]. J Am Chem Soc 2008;130:10044–5.

[32] Schneider J, Lee YA, Pérez J, Brennessel WW, Flaschenriem C, Eisenberg R. Strong intra- and intermolecular aurophilic interactions in a new series of brilliantly luminescent dinuclear cationic and neutral Au(I) benzimidazolethiolate complexes. Inorg Chem 2008;47:957–68.

[33] Catalano VJ, Horner SJ. Luminescent gold(I) and silver(I) complexes of 2-(diphenylphosphino)-1-methylimidazole (dpim): characterization of a three-coordinate Au(I)–Ag(I) dimer with a short metal-metal separation. Inorg Chem 2003;42:8430–8.

[34] Assefa Z, Omary MA, McBurnett BG, Mohamed AA, Patterson HH, Staples RJ, et al. Syntheses, structure, and photoluminescence properties of the 1-dimensional chain compounds $[(TPA)_2Au][Au(CN)_2]$ and (TPA)AuCl (TPA = 1,3,5-Triaza-7-phosphaadamantane). Inorg Chem 2002;41:6274–80.

[35] Lee YA, Eisenberg R. Luminescence tribochromism and bright emission in gold(I) thiouracilate complexes. J Am Chem Soc 2003;125:7778–9.

[36] Mizukami S, Houjou H, Sugaya K, Koyama E, Tokuhisa H, Sasaki T, et al. Fluorescence color modulation by intramolecular and intermolecular $\pi-\pi$ interactions in a helical zinc(II) complex. Chem Mater 2005;17:50–6.

[37] Tsukuda T, Kawase M, Dairiki A, Matsumoto K, Tsubomura T. Brilliant reversible luminescent mechanochromism of silver(I) complexes containing o-bis(diphenylphosphino)benzene and phosphinesulfide. Chem Commun 2010;46:1905–7.

[38] Ni J, Zhang X, Wu YH, Zhang LY, Chen ZN. Vapor- and mechanical-grinding-triggered color and luminescence switches for bis(σ-fluorophenylacetylide) platinum(II) complexes. Chem Eur J 2011;17:1171–83.

[39] Ni J, Zhang X, Qiu N, Wu YH, Zhang LY, Zhang J, et al. Mechanochromic luminescence switch of platinum(II) complexes with 5-trimethylsilylethynyl-2,2’-bipyridine. Inorg Chem 2011;50:9090–6.

[40] Abe T, Itakura T, Ikeda N, Shinozaki K. Luminescence color change of a platinum(II) complex solid upon mechanical grinding. Dalton Trans 2009;4:711–5.

[41] Perruchas S, Goff XFL, Maron S, Maurin I, Guillen F, Garcia A, et al. Mechanochromic and thermochromic luminescence of a copper iodide cluster. J Am Chem Soc 2010;132:10967–9.

[42] Shan GG, Li HB, Cao HT, Zhu DX, Li P, Su ZM, et al. Reversible piezochromic behavior of two new cationic iridium(III) complexes. Chem Commun 2012;48: 2000–2.

[43] Shan GG, Li HB, Zhu DX, Su ZM, Liao Y. Intramolecular π-stacking in cationic iridium(III) complexes with a triazole-pyridine type ancillary ligand: synthesis, photophysics, electrochemistry properties and piezochromic behavior. J Mater Chem 2012. http://dx.doi.org/10.1039/C2JM30480E.

[44] Szerb EI, Talarico AM, Aiello I, Crispini A, Godbert N, Pucci D, et al. Red to green switch driven by order in an ionic Ir^{III} liquid-crystalline complex. Eur J Inorg Chem 2010;21:3270–7.

[45] Bi H, Chen D, Li D, Yuan Y, Xia DD, Zhang ZL, et al. A green emissive amorphous *fac*-Alq3 solid generated by grinding crystalline blue *fac*-Alq$_3$ powder. Chem Commun 2011;47:4135–7.

[46] Uson R, Laguna A, Laguna M. (Tetrahydrothiophene)gold(I) or gold(III) complexes. Inorg Synth 1989;26:85–91.

[47] Yamamotoa Y, Yamamotoa H, Tajima N, Tatsumi K. Stepwise formation of quasi-octahedral macrocyclic complexes of rhodium(III) and iridium(III) bearing a pentamethylcyclopentadienyl group. Chem Eur J 2002;8:372–9.

[48] Huang JB, Lin R, Wu LQ, Zhao QY, Zhu CQ, Wen TB, et al. Synthesis, characterization, and electrochemical properties of bisosmabenzenes bridged by diisocyanides. Organometallics 2010;29:2916–25.

[49] Liu GB, Zhao HY, Lu D, Thiemann T, Tashiro H, Tashiro M. Raney Ni-Al alloy-mediated reduction of benzils in water. J Chem Res 2009;9:579–81.

[50] Sheldrick GM. SHELXS-97, a program for crystal structure solution. Germany: Göttingen; 1997.

[51] Sheldrick GM. SHELXL-97, a program for crystal structure refinement. Germany: Göttingen; 1997.

[52] Schmidbaur H. The aurophilicity phenomenon: a decade of experimental findings, theoretical concepts and emerging applications. Gold Bulletin 2000; 33:3–10.

[53] Gagnon J, Drouin M, Harvey PD. Upper-rim functionalization of calix[4]arene by chloro(isocyanide)gold(I) groups: an entry to polymetallic architecture. Inorg Chem 2001;40:6052–6.

[54] Muller TE, Choi SWK, Mingos DMP, Murphy D, Williams DJ, Yam VWW. Synthesis, structural characterization and photophysical properties of ethyne-gold(I) complexes. J Organomet Chem 1994;484:209–24.