Supporting information for:

A twisted tetra-gold cyclophane from a fused bis-imidazolin-di-ylidene

by

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General considerations. 2,4,6,8-Tetraazabicyclo[3.3.0]octane,^[1] [AuCl(SMe)₂]^[2] and 3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole^[3] were prepared according to the reported literature methods. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Bruker 400 or 300 MHz, using CDCl₃ or DMSO-d₆ as solvents. Infrared spectra (FTIR) were performed on a Bruker Equinox 55 spectrometer equipped with a Pro One ATR (Jasco) with a spectral window of 4000-400 cm⁻¹. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. High Resolution Mass Spectra (HRMS) were recorded on a Q-TOF Premier mass spectrometer (Waters) with an electrospray source operating in the V-mode. Nitrogen was used as the drying and cone gas at flow rates of 300 and 30 Lh⁻¹, respectively. The temperature of the source block was set to 120°C, and the desolvation temperature was set to 150°C. Capillary voltage of 3.5 kV was used in the positive scan modes and the cone voltage was adjusted typically to 20 V. Mass calibration was performed by using solutions of NaI in isopropanol/water (1:1) from m/z 50 to 3000. Elemental analyses were carried out on a TruSpec Micro Series. UV-Visible absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer using dichloromethane under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog-3 spectrofluorometer employing dichloromethane. PLQY was measured using a Hamamatsu integrating sphere at excitation wavelength of 315 nm.

1. Synthesis of the Au(I) complexes

1.1. Synthesis of the bis-imidazolidinium salt 1. N-Chlorosuccinimide (0.8 g, 6.3 mmol, 3 eq.) was slowly added to a solution of 2,4,6,8-tetraazabicyclo[3.3.0]octane (1.0 g, 2.1 mmol, 1 eq.) in degassed 1,2-dimethoxyethane (DME, 15 mL) at 0°C. The resulting solution was allowed to reach room temperature and then stirred for 18 h under the exclusion of light. The solid so formed was filtrated and washed subsequently with cold dichloromethane, THF and acetone. Yield: 77.8 mg (68 %). Electrospray MS (20 V, *m/z*): 503.5 [1–(2Cl)+OMe]⁺ (calcd. for [1–(2Cl)+OMe]⁺: 503.3), 236.2 [1–(2Cl)]²⁺ (calcd. for [1–(2Cl)+OMe]⁺: 503.3), 236.2 [1–(2Cl)]²⁺ (calcd. for [1–(2Cl)]²⁺: 236.1). Anal. Calcd. for C₃₂H₃₂N₄Cl₂ (542.9): C, 70.71; H, 5.93; N, 10.31. Found: C, 69.98; H, 5.90; N, 10.28. ¹H NMR (300 MHz, 298 K, DMSO-*d*₆): δ 9.51 (s, 2H, C*H*), 7.42-7.38 (m, 20H, C*H*_{Ph}), 6.53 (s, 2H, C*H*_{bridge}), 5.03 (d, ²*J*_{H-H} = 15 Hz, 4H, C*H*_{2 Ph}). ¹³C NMR (75 MHz, 298 K, DMSO-*d*₆):

 δ 162.32 (NCHN), 132.55 (C_q Ph), 128.92 (CH_{Ph}), 128.83 (CH_{Ph}), 128.63 (CH_{Ph}), 81.65 (CH_{bridge}), 51.03 (CH_2 Ph).

1.2. Synthesis of di-Au(I) complex 2. KHMDS (0.5M in toluene, 0.8 mL, 0.405 mmol, 2.2 eq.) was added dropwise to a suspension of compound 1 (100.0 mg, 0.184 mmol, 1 eq.) in THF (5 mL) at -78°C. After stirring at that temperature for 30 minutes, the resulting solution was transferred via an oven dried cannula to a stirred THF solution (10 mL) of [AuCl(SMe)₂] (119.2 mg, 0.405 mmol, 2.2 eq.). The temperature was allowed to reach -20°C, and then the volatiles were removed under reduced pressure. The resulting solid was suspended in dichloromethane. Under air, a spatula of charcoal was added and the mixture was stirred for 30 minutes. The suspension was then filtered through oven dried Celite, washed with dichloromethane and the solvent was removed under vacuum. The solid was dissolved in the minimum amount of dichloromethane and precipitated with diethyl ether to afford the desired gold(I) complex as a white solid. Yield: 122.0 mg (69 %). Complex 2 was found light sensitive, which prevented a correct elemental analysis. ¹H NMR (400 MHz, 298 K, CDCl₃): δ7.38-7.31 (m, 14H, CH_{Ph}), 7.13-7.06 (m, 6H, CH_{Ph}), 5.56 (d, ${}^{2}J_{H-H}$ = 16 Hz, 4H, $CH_{2 Ph}$), 5.35 (s, 2H, CH_{bridge}), 4.54 (d, ${}^{2}J_{H-H}$ = 16 Hz, 4H, CH_{2 Ph}). ¹³C NMR (100 MHz, 298 K, CDCl₃): δ198.40 (Au-C_{carbene}), 133.01 (C_{g Ph}), 129.71 (CH_{Ph}), 129.38 (CH_{Ph}), 127.38 (CH_{Ph}), 79.72 (CH_{bridge}), 54.20 (CH_{2 Ph}).

1.3. Synthesis of tetra-Au(I) complex **3**. NaOH (22.45 mg, 0.561 mmol, 3.5 eq.) and 3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole (52.5 mg, 0.160 mmol, 1 eq.) were placed together in a Schlenk tube. The tube was evacuated and filled with nitrogen three times. The solids were suspended in degassed MeOH (50 mL), and the resulting solution was refluxed for 2 h. After this time, the solution was allowed to reach room temperature. Complex **2** (150.0 mg, 0.160 mmol, 1eq.) was added to the latter solution and the resulting suspension was refluxed overnight. The suspension was allowed to reach room temperature. After removal of the volatiles, the crude solid was suspended in dichloromethane and filtered through oven dried Celite. Complex **3** was isolated as a yellow solid. Yield: 129.4 mg (62 %). IR (ATR): v(C=C): 2099, 2090 cm⁻¹. HRMS ESI-TOF-MS (positive mode): 2381.0 [**3**+H]⁺. (Calcd. for [**3**+H]⁺: 2380.7). Anal. Calcd. for $C_{112}H_{106}N_{10}Au_4$ (2379.72): C, 56.52; H, 4.49; N, 5.89. Found: C, 56.62; H, 4.70; N, 5.92. ¹H NMR (400 MHz, 298 K, CDCl₃): δ 8.81 (s, 2H, NH), 7.87 (d, ⁴J_{H-H} = 1.7 Hz, 4H, *CH*_{carb}), 7.58 (d, ⁴J_{H-H} = 1.7 Hz, 4H, *CH*_{carb}), 7.58 (d, ⁴J_{H-H} = 1.7 Hz, 4H, *CH*_{carb}), 7.38-7.36 (dd, ²J_{H-H} = 3 Hz, 28H, *CH*_{Ph}),

7.20-7.18 (m, 12H, CH_{Ph}), 5.89 (d, ${}^{2}J_{H-H}$ = 16 Hz, 8H, CH_{2 Ph}), 5.35 (s, 4H, CH_{bridge}), 4.62 (d, ${}^{2}J_{H-H}$ = 16 Hz, 8H, CH_{2 Ph}), 1.36 (s, 36H, C(CH₃)_{3 carb}). 13 C NMR (75 MHz, 298 K, CDCl₃): δ 189.92 (Au-C_{carben}), 141.90 (C_{q carb}), 139.09 (C_{q carb}), 133.38 (C_{q Ph}), 129.61 (CH_{Ph}), 129.22 (CH_{Ph}), 128.93 (C_{q carb}), 128.08 (CH_{carb}), 127.68 (CH_{Ph}), 122.94 (C_{q acetyl}), 118.03 (C_{q acetyl}), 115.64 (CH_{carb}), 107.12 (C_{q carb}), 79.79 (CH_{bridge}), 53.90 (CH_{2 Ph}), 34.76 (C(CH₃)_{3 carb}), 32.08 (C(CH₃)_{3 carb}).

2. Spectroscopic data

Figure S1. ¹H NMR spectrum (300 MHz, DMSO-*d*₆) of bis-imidazolidinium salt 1

Figure S2. ¹³C NMR spectrum (75 MHz, DMSO- d_6) of bis-imidazolidinium salt 1

Figure S4. ¹³C NMR spectrum (100 MHz, CDCl₃) of di-Au(I) complex 2

Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃) of tetra-Au(I) complex 3

Figure S6. ¹³C NMR spectrum (100 MHz, CDCl₃) of tetra-Au(I) complex 3

Figure S7. HMBC spectrum (400 MHz, CDCl₃) of tetra-Au(I) complex 3

3. X-Ray crystallography

X-Ray Diffraction studies for complexes 2 and 3. Crystals suitable for X-Ray studies of complex **2** were obtained by slow evaporation of a concentrated solution of the complex in chloroform. Suitable crystals of complex **3** were obtained by slow diffusion of hexane into a concentrated solution of the complex in dichlorometane. Diffraction data of complexes were collected on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-K α radiation ($\lambda = 0.71073$ Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multi-scan method were applied. Using Olex2,^[4] the structure of the two complexes was solved using Charge Flipping in Superflip^[5-6] and refined with ShelXL^[7] refinement package using Least Squares minimisation. Key details of the crystals and structure refinement data are summarized in Supplementary Table S1. Further crystallographic details can be found in the CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The reference numbers for complexes **2** and **3** were assigned as 1961185 and 1961186, respectively.

| | complex 2 | complex 3 |
|------------------------------|----------------------------------|-----------------------------------|
| Empirical formula | $C_{132}H_{30}Au_2N_4Cl_2+2/3$ | $C_{123}H_{117}Au_4Cl_{33}N_{10}$ |
| Empirical formula | (CH_2Cl_2) | |
| Formula weight | 963.73 | 3692.98 |
| Temperature/K | 200(2) | 200(4) |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/n$ | P-1 |
| a/Å | 13.9652(8) | 11.6839(5) |
| b/Å | 28.6096(19) | 14.7840(7) |
| c/Å | 16.5811(13) | 22.4048(8) |
| $\alpha/^{\circ}$ | 90 | 86.592(3) |
| β/° | 101.169(7) | 75.809(3) |
| $\gamma/^{\circ}$ | 90 | 81.581(4) |
| Volume/Å ³ | 6499.3(8) | 3710.4(3) |
| Z | 8 | 1 |
| $\rho_{calcg}\!/cm^3$ | 1.970 | 1.653 |
| μ/mm^{-1} | 9.266 | 4.583 |
| F(000) | 3648.0 | 1802.0 |
| Crystal size/mm ³ | $0.585 \times 0.12 \times 0.098$ | $0.691 \times 0.064 \times 0.053$ |

Table S1. Summary of crystal data, data collection, and structure refinement details

| 20 range for data collection | 5.11 to 52.744 | 5.018 to 52.68 |
|--|------------------------------|------------------------------|
| | $-17 \le h \le 17$, | $-14 \le h \le 14$, |
| Index ranges | $-34 \le k \le 35,$ | $-18 \le k \le 18,$ |
| | $-20 \le l \le 20$ | $-27 \le l \le 24$ |
| Reflections collected | 56401 | 29024 |
| Independent | 56401 [$R_{int} = 0.0467$, | 29024 [$R_{int} = 0.0252$, |
| reflections | $R_{sigma} = 0.0953$] | $R_{sigma} = 0.1300$] |
| Data/restraints/ | 56401/12/748 | 29024/654/817 |
| parameters | 00101/12//10 | |
| Goodness-of-fit on F ² | 1.031 | 1.016 |
| Final R indexes | $R_1 = 0.0787,$ | $R_1 = 0.0895,$ |
| [I>=2σ (I)] | $wR_2 = 0.1917$ | $wR_2 = 0.2301$ |
| Final R indexes | $R_1 = 0.1249,$ | $R_1 = 0.1268,$ |
| [all data] | $wR_2 = 0.2323$ | $wR_2 = 0.2673$ |
| Largest diff. peak/hole / e Å ⁻³ | 9.56/-4.82 | 4.48/-2.92 |

4. DOSY experiment

Figure S8. Diffusion Ordered NMR Spectrum (DOSY) of complex 3 (5 mM) in CDCl₃.

5. Photophysical studies

5.1. UV-visible spectra of complex 3

Figure S9. UV-vis spectra of complex **3**, recorded in dichloromethane at a concentration of 10⁻⁵ M, under aerobic conditions

5.2. Emission spectra of complex 3

Figure S10. Emission spectra of complex 3 in dichloromethane (10⁻⁵ M under aerobic conditions) at 315 nm

6. References

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