A Chiral Luminescent Au_{16} Ring Self-Assembled from Achiral Components

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Supporting Information

*Synthesis of **1**$_4$*

To a suspension of [(dppm)$AuCl_2$] (34 mg, 0.04 mmol) in anhydrous MeOH (2 mL), K_2(pipzdtc) (6.3 mg, 0.02 mmol) in anhydrous MeOH (3 mL) was added and the mixture was stirred at room temperature for 2 hours until it became clear. An excess of NH_4PF_6 (26 mg, 0.16 mmol) was added to the resulting yellow solution, from which the product was precipitated instantly as a yellow solid. Recrystallization from CH_3CN/MeOH/Et_2O yielded **1**$_4$ as yellow crystals (29 mg, 70 %). ^{1}H NMR (dmso-d_6, 400 MHz, 298 K, relative to $SiMe_4$, ppm): δ = 7.73-7.37 (m, 40H, Ph); 4.80 (t, 4H, ^2J(HP) = 13.3 Hz, PCH_2); 4.52 (br, 8H, CH_2 of pipzdtc). ESI-MS: m/z = 896.8, $[(dppm)_2Au_4(pipzdtc)]^{2+}$. IR (KBr): ν (cm^{-1}) = 3439, 1625, 1480 (C-N), 1436, 1415, 1355, 1275, 1209, 1144, 1102, 1025, 997, 841 (PF_6^-), 781, 743, 692. Anal. Calcd for $C_{224}H_{208}Au_{16}F_{48}N_8P_{24}S_{16}$ (8331.69): C, 32.29; H, 2.52; N, 1.34; S, 6.16. Found: C, 32.15; H, 2.34; N, 1.37; S, 6.03.

*X-ray crystallography of **1**$_4$*

The single crystal of **1**$_4$ was obtained by slow diffusion of diethyl ether vapor into a MeCN/MeOH (1:1 v/v) solution of **1**. A yellow single crystal with dimensions of 0.24×0.26×0.32 mm was sealed in a glass capillary and mounted on a Bruker Smart Aepex CCD area detector equipped with a graphite monochromated MoKα radiation. The data was collected at 293(2) K. The structure was solved by direct methods by using SHELXTL (Bruker, 2000) program and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed at the ideal positions.

*Solid-state CD experiment for **1**$_4$*

A MeCN/MeOH (1:1 v/v) solution of **1** (6.67×10^{-3} M, 15 ml) was placed into ten small glass tubes and the tubes were allowed to stand without stirring at room temperature with diethyl ether vapor slowly diffusing into each tube. Then, ten pieces of single crystals of **1**$_4$ were randomly picked from each tube. Each crystal (~2×1×0.5 mm) was ground with ~ 2 mg of liquid paraffin and the resulting Nujol mull was sandwiched between two quartz plates for CD measurements. The crystals exhibited CD spectra (a or b) with an exciton-coupled split Cotton effect, as shown in Figure 2a. As far as the single crystals from the same tube were concerned, about 7 pieces of which showed the same chirality while the remaining 3 pieces showed the opposite chirality with a similar intensity but opposite sign. The two curves were mirror images of each other.

Table 1. Crystal structure determination data for **1**$_4$

Formula	$C_{224}H_{208}Au_{16}F_{48}N_8P_{24}S_{16}$
Formula Weight	8331.69
Crystal System	Monoclinic
Space group	$P2_1$ (No. 4)
a [Å]	26.969(5)
b [Å]	26.417(5)
c [Å]	24.926(5)
α [deg]	90
β [deg]	117.095(5)
γ [deg]	90
V [Å^3]	15809(5)
Z	2
D_{calc} [g cm^{-3}]	1.750
μ(Mo Kα) [mm^{-1}]	7.688
F(000)	7840
Crystal Size [mm]	$0.24 \times 0.26 \times 0.32$
T [K]	293(2)
λ [Å] (graphite monochromated, Mo Kα)	0.71073
θ range [Deg]	1.8 to 27.0
Data range	h: –34 to 29; k: –33 to 33; l: –25 to 31
No. of reflections collected	91601
No. of independent reflections	62007 (R_{int} = 0.028)
Observed data [$I > 2\sigma(I)$]	49554
No. of data used in refinement	62007
No. of parameters	3026
R [$I > 2\sigma(I)$]	0.0489
wR_2 [$I > 2\sigma(I)$][a]	0.1241
S	1.002
Flack x	0.107(4)
Largest diff. peak and hole [e Å^{-3}]	4.21, –5.16

[a] $w = 1 / [\sigma^2(F_0^2) + (0.08P)^2 + 1.65P]$, where $P = (F_0^2 + 2F_c^2) / 3$

Table 2. Selected bond distances (Å) for **1**$_4$

Au(1)-Au(2)	2.9073(8)	Au(5)-P(5)	2.238(4)
Au(1)-Au(16)	3.2151(8)	Au(5)-S(5)	2.288(3)
Au(2)-Au(3)	3.1020(8)	Au(6)-P(6)	2.246(3)
Au(3)-Au(4)	2.8981(7)	Au(6)-S(6)	2.285(3)
Au(4)-Au(5)	3.1329(8)	Au(7)-P(7)	2.294(3)
Au(5)-Au(6)	2.9078(7)	Au(7)-S(7)	2.309(3)
Au(6)-Au(7)	3.0929(7)	Au(8)-P(8)	2.271(3)
Au(7)-Au(8)	2.9026(8)	Au(8)-S(8)	2.317(3)
Au(8)-Au(9)	3.1234(8)	Au(9)-P(9)	2.260(4)
Au(9)-Au(10)	2.9091(8)	Au(9)-S(9)	2.300(3)
Au(10)-Au(11)	3.1233(7)	Au(10)-P(10)	2.274(3)
Au(11)-Au(12)	2.9025(9)	Au(10)-S(10)	2.327(3)
Au(12)-Au(13)	3.1129(9)	Au(11)-P(11)	2.269(4)
Au(13)-Au(14)	2.8947(7)	Au(11)-S(11)	2.317(4)
Au(14)-Au(15)	3.0863(8)	Au(12)-P(12)	2.272(3)
Au(15)-Au(16)	2.9087(8)	Au(12)-S(12)	2.314(3)
Au(1)-P(1)	2.254(3)	Au(13)-P(13)	2.259(3)
Au(1)-S(1)	2.310(2)	Au(13)-S(13)	2.299(3)
Au(2)-P(2)	2.245(3)	Au(14)-P(14)	2.278(3)
Au(2)-S(2)	2.307(3)	Au(14)-S(14)	2.305(3)
Au(3)-P(3)	2.311(3)	Au(15)-P(15)	2.288(3)
Au(3)-S(3)	2.313(3)	Au(15)-S(15)	2.334(3)
Au(4)-P(4)	2.266(3)	Au(16)-P(16)	2.267(4)
Au(4)-S(4)	2.315(3)	Au(16)-S(16)	2.300(4)

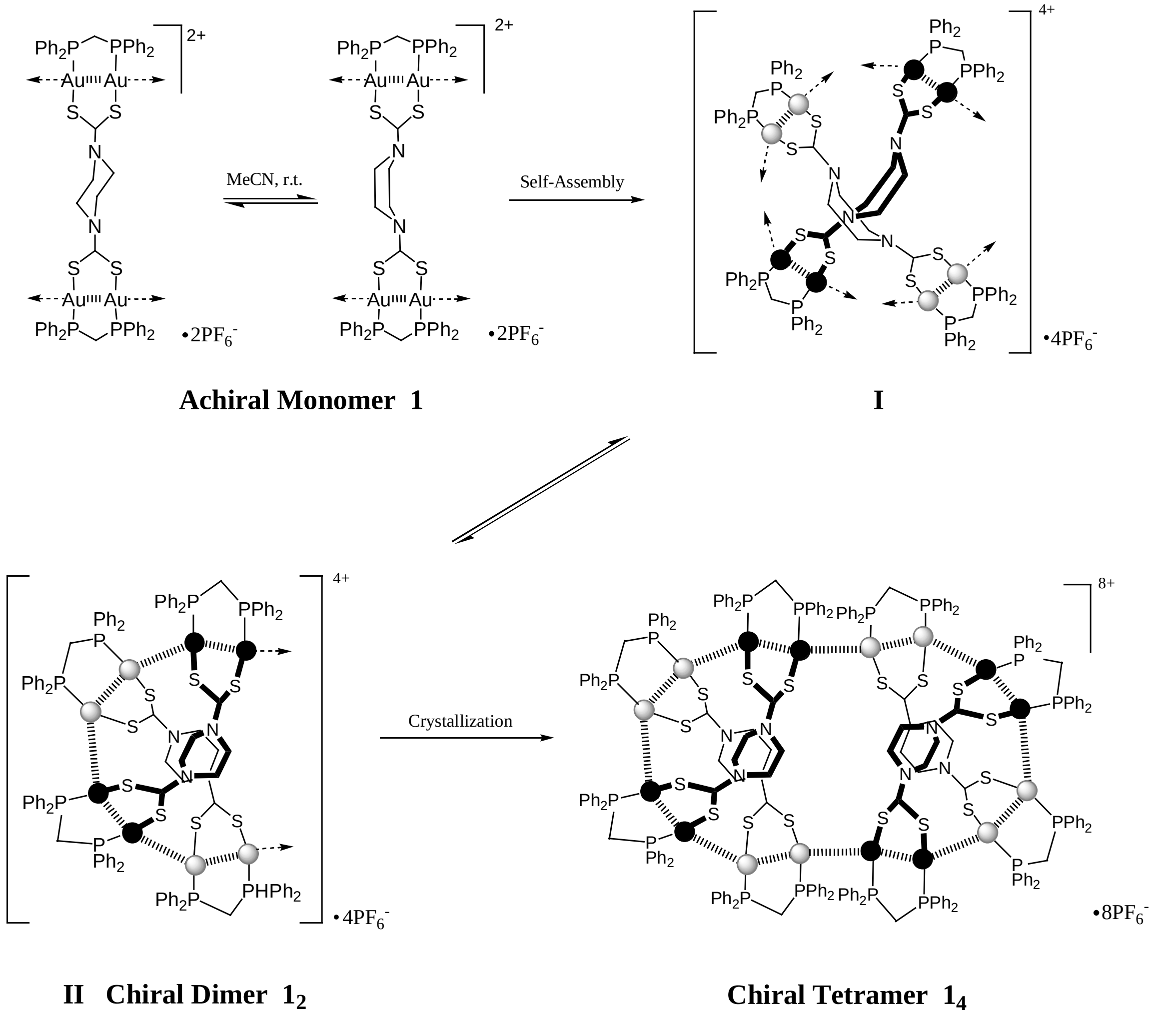
Table 3. Selected bond angles (deg) for **1**$_4$

P(1)-Au(1)-S(1)	171.65(8)	P(9)-Au(9)-S(9)	174.40(10)
P(1)-Au(1)-Au(2)	83.68(8)	P(9)-Au(9)-Au(10)	86.27(10)
S(1)-Au(1)-Au(2)	88.03(7)	S(9)-Au(9)-Au(10)	88.26(8)
P(1)-Au(1)-Au(16)	101.15(8)	P(9)-Au(9)-Au(8)	98.41(9)
S(1)-Au(1)-Au(16)	87.20(7)	S(9)-Au(9)-Au(8)	86.82(8)
Au(2)-Au(1)-Au(16)	171.33(2)	Au(10)-Au(9)-Au(8)	170.08(2)
P(2)-Au(2)-S(2)	163.34(8)	P(10)-Au(10)-S(10)	167.83(7)
P(2)-Au(2)-Au(1)	99.57(8)	P(10)-Au(10)-Au(9)	92.05(8)
S(2)-Au(2)-Au(1)	90.53(7)	S(10)-Au(10)-Au(9)	91.22(7)
P(2)-Au(2)-Au(3)	102.87(8)	P(10)-Au(10)-Au(11)	109.28(8)
S(2)-Au(2)-Au(3)	80.13(8)	S(10)-Au(10)-Au(11)	78.73(8)
Au(1)-Au(2)-Au(3)	129.80(2)	Au(9)-Au(10)-Au(11)	121.69(2)
P(3)-Au(3)-S(3)	169.72(9)	P(11)-Au(11)-S(11)	171.15(10)
P(3)-Au(3)-Au(4)	91.28(7)	P(11)-Au(11)-Au(12)	92.50(9)
S(3)-Au(3)-Au(4)	89.87(8)	S(11)-Au(11)-Au(12)	88.37(10)
P(3)-Au(3)-Au(2)	110.77(9)	P(11)-Au(11)-Au(10)	105.86(7)
S(3)-Au(3)-Au(2)	76.94(7)	S(11)-Au(11)-Au(10)	79.56(8)
Au(4)-Au(3)-Au(2)	122.94(2)	Au(12)-Au(11)-Au(10)	134.24(2)
P(4)-Au(4)-S(4)	175.49(7)	P(12)-Au(12)-S(12)	175.36(9)
P(4)-Au(4)-Au(3)	87.12(7)	P(12)-Au(12)-Au(11)	88.57(9)
S(4)-Au(4)-Au(3)	88.62(7)	S(12)-Au(12)-Au(11)	86.80(8)
P(4)-Au(4)-Au(5)	91.50(7)	P(12)-Au(12)-Au(13)	94.38(9)
S(4)-Au(4)-Au(5)	92.39(7)	S(12)-Au(12)-Au(13)	90.26(8)
Au(3)-Au(4)-Au(5)	168.76(2)	Au(11)-Au(12)-Au(13)	177.05(2)

P(5)-Au(5)-S(5)	172.90(7)	P(13)-Au(13)-S(13)	172.81(9)
P(5)-Au(5)-Au(6)	89.24(9)	P(13)-Au(13)-Au(14)	88.47(9)
S(5)-Au(5)-Au(6)	88.30(7)	S(13)-Au(13)-Au(14)	89.51(7)
P(5)-Au(5)-Au(4)	113.50(7)	P(13)-Au(13)-Au(12)	115.99(9)
S(5)-Au(5)-Au(4)	73.46(7)	S(13)-Au(13)-Au(12)	70.63(8)
Au(6)-Au(5)-Au(4)	119.51(2)	Au(14)-Au(13)-Au(12)	125.92(2)
P(6)-Au(6)-S(6)	176.31(7)	P(14)-Au(14)-S(14)	175.05(10)
P(6)-Au(6)-Au(5)	93.37(8)	P(14)-Au(14)-Au(13)	93.73(10)
S(6)-Au(6)-Au(5)	88.09(8)	S(14)-Au(14)-Au(13)	81.33(9)
P(6)-Au(6)-Au(7)	104.30(8)	P(14)-Au(14)-Au(15)	100.90(10)
S(6)-Au(6)-Au(7)	75.39(8)	S(14)-Au(14)-Au(15)	83.94(9)
Au(5)-Au(6)-Au(7)	155.02(2)	Au(13)-Au(14)-Au(15)	158.26(2)
P(7)-Au(7)-S(7)	173.58(9)	P(15)-Au(15)-S(15)	166.94(9)
P(7)-Au(7)-Au(8)	94.45(8)	P(15)-Au(15)-Au(16)	97.73(8)
S(7)-Au(7)-Au(8)	87.00(8)	S(15)-Au(15)-Au(16)	89.59(8)
P(7)-Au(7)-Au(6)	95.24(8)	P(15)-Au(15)-Au(14)	101.03(8)
S(7)-Au(7)-Au(6)	87.97(8)	S(15)-Au(15)-Au(14)	81.04(8)
Au(8)-Au(7)-Au(6)	136.30(2)	Au(16)-Au(15)-Au(14)	134.60(2)
P(8)-Au(8)-S(8)	170.56(10)	P(16)-Au(16)-S(16)	159.11(9)
P(8)-Au(8)-Au(7)	86.75(9)	P(16)-Au(16)-Au(15)	86.65(9)
S(8)-Au(8)-Au(7)	88.05(8)	S(16)-Au(16)-Au(15)	85.65(7)
P(8)-Au(8)-Au(9)	117.59(9)	P(16)-Au(16)-Au(1)	125.98(9)
S(8)-Au(8)-Au(9)	71.64(8)	S(16)-Au(16)-Au(1)	72.76(8)
Au(7)-Au(8)-Au(9)	131.43(2)	Au(15)-Au(16)-Au(1)	131.09(2)

Table 4. Luminescence data for $\{[(dppm)_2Au_4(pipzdtc)]^{2+}\}_n$

Complex	Medium (T / K)	n (conc. / M)	λ_{em} / nm	τ_0 / µs
$[(dppm)_2Au_4(pipzdtc)](PF_6)_2$ **1**	Solid (293)	4 (---)	531	< 0.1
	Solid (77)	4 (---)	524	3.0, 12.2
	MeCN (293)	1 (5.0×10^{-5})	608	14.9
	Me_2CO (293)	1 (4.0×10^{-5})	605	16.0
	^{n}PrCN (77)	1 (6.2×10^{-5})	501	2.6, 5.9
$[(dppm)_2Au_4(pipzdtc)](BF_4)_2$	MeCN (293)	1 (4.8×10^{-5})	605	13.6
$[(dppm)_2Au_4(pipzdtc)](ClO_4)_2$	MeCN (293)	1 (4.2×10^{-5})	609	19.3



Scheme S1. Proposed chiral self-assembly process for the formation of the chiral macrocyclic tetramer $\mathbf{1}_4$ from the achiral monomer **1** through Au(I)···Au(I) interactions. I and II represent two proposed intermediates in the stage of the assembly. ● and ○ represent the gold(I) centers. The dotted arrows attached to Au_2 units represent the orientation of Au(I)···Au(I) interactions. In the self-assembly process, the boat conformation of pipz in **1** is preferred.