Supplementary Material (ESI) for Chemical Communications

Supplementary Information

For

Luminescent gold(III) organometallic complex of N-confused tetraphenylporphyrin

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General. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. NBS was recrystallized from hot water. Toluene was distilled over CaH_2. $AuCl{\bullet}SMe_2$ is freshly prepared from $HAuCl_4{\bullet}4H_2O$ and Me_2S in MeOH. Thin-layer chromatography (TLC) was carried out on aluminium sheets coated with silica gel 60 (Merck 5554). Preparative purifications were performed by flash column chromatography (KANTO Silica Gel 60 N, spherical, neutral, 40–50 μm) or gravity column chromatography (KANTO Silica Gel 60 N, spherical, neutral, 63–210 μm). The ^{1}H NMR or ^{13}C NMR spectra were recorded on a JNM-AI SERIES FT-NMR spectrometer (JEOL) at 300 MHz or 75 MHz, respectively. Proton chemical shifts were reported relative to residual proton of deuterated solvent (δ 7.26 ppm for $CHCl_3$). Carbon chemical shifts were reported relative to $CDCl_3$ at δ 77.00 ppm. UV-vis absorption spectra were recorded on a UV-3150PC spectrometer (Shimadzu). Emission spectra were recorded on an SPEX Fluorolog spectrometer (HORIBA). Mass spectra were recorded on an autoflex MALDI-TOF MS spectrometer (Bruker Daltonics). Cyclic voltammetric measurements were performed on a CH Instrument Model 620B (ALS) equipped with a Pt electrode.

Synthesis of AuNCTPP (3)

A mixture of 21-Br-NCTPP (16.6 mg, 23.9 μmol, 1 equiv) and $AuCl{\bullet}SMe_2$ (23.1 mg, 78.4 μmol, 3.3 equiv) in toluene was refluxed for 11 h. The resulting mixture was dried under reduced pressure and the residue was purified by silica gel column chromatography ($MeOH/CH_2Cl_2$ = 1/100) to give **3** in 37% yield (7.1 mg, 8.8 μmol). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.72–7.77 (m, 12H), 8.08–8.19 (m, 8H), 8.64 (d, J =

5.2 Hz, 1H), 8.66 (d, J = 5.2 Hz, 1H), 8.68 (d, J = 4.9 Hz, 1H), 8.70 (d, J = 4.9 Hz, 1H), 8.86 (d, J = 5.2 Hz, 1H), 8.94 (d, J = 5.2 Hz, 1H), 9.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 104.07, 119.49, 120.64, 125.46, 126.80, 126.97, 127.13, 127.17, 127.21, 127.61, 127.93, 127.98, 128.12, 129.05, 129.49, 129.62, 129.94, 130.42, 131.18, 133.73, 133.79, 134.09, 134.21, 136.67, 137.53, 138.32, 138.45, 138.87, 139.52, 139.86, 139.93, 141.00, 141.59, 164.40; HRMS (ESI+) m/z: found: 809.19395, calcd for $C_{44}H_{28}N_4Au$ (MH^+): 809.19795; UV-vis (CH_2Cl_2, λ_{max}/nm (ε)): 435 (144000), 513 (15400), 549 (5600), 636 (8700).

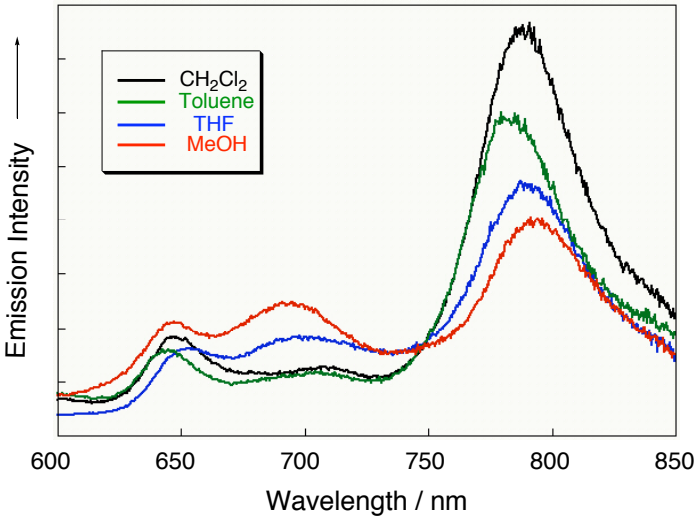

Fig. S1 Emission spectra of **3** at room temperature (excited at 435 nm).

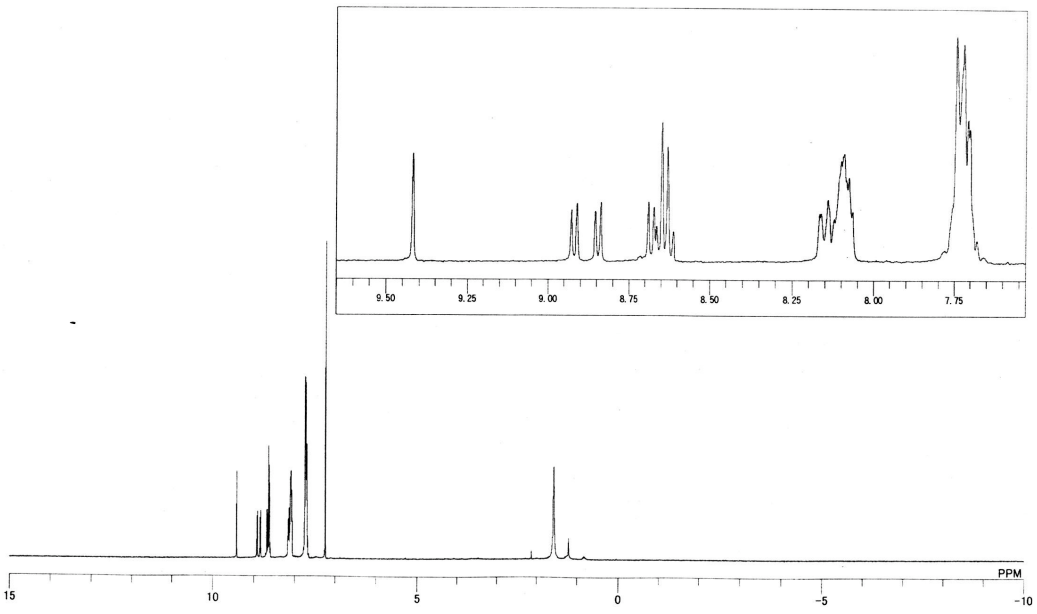

Fig. S2 ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature.

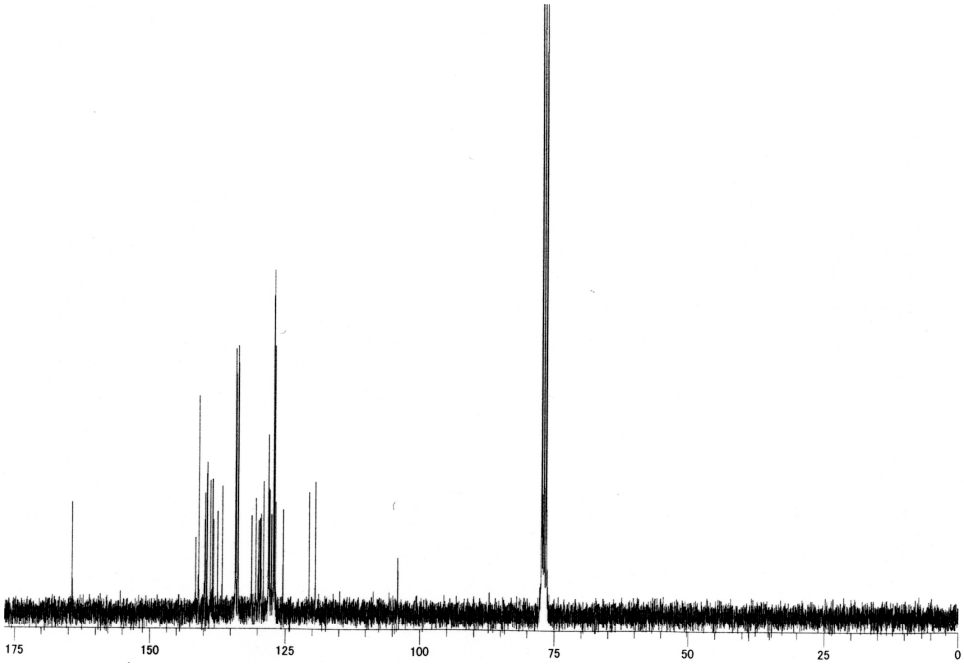

Fig. S3 ^{13}C NMR spectrum of **3** in $CDCl_3$ at room temperature.

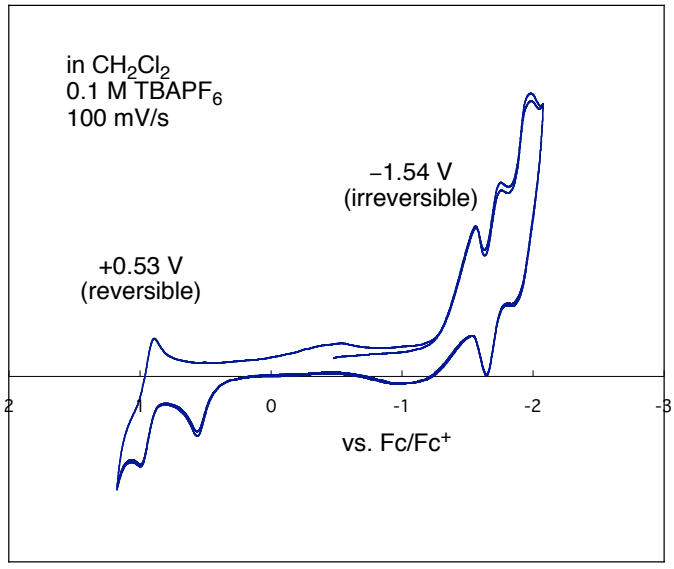

Fig. S4 Cyclic voltammogram of **3** at room temperature.

Calculation details. All the DFT calculations were performed with a Gaussian 03 program package[1] without symmetry assumption. The geometries were fully optimized at the Becke's three-parameter hybrid functional[2] combined with the Lee-Yang-Parr correlation functional[3] abbreviated as the B3LYP level of density functional theory. The SDD basis set[4] was used for Au and the 6-31G** basis sets for C, H and N. This combination was denoted as 631S. The stationary points are verified by the frequency calculations.

Optimized structure of 3 at B3LYP/631S level

Stoichiometry C44H27AuN4
Framework group C1[X(C44H27AuN4)]
Deg. of freedom 222
Full point group C1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	-0.002247	-0.003455	-0.009040
2	6	0	-4.041952	-1.258604	-0.049437
3	6	0	-2.610535	-1.582701	-0.034149
4	6	0	-2.030828	-2.858458	-0.048610
5	6	0	-0.637712	-3.037406	-0.029764
6	6	0	0.039383	-4.300370	0.004031
7	6	0	1.380970	-4.056502	0.037345
8	6	0	1.568336	-2.632634	0.037857
9	6	0	2.827983	-2.004766	0.073742
10	6	0	3.042955	-0.623042	0.051247
11	6	0	4.330016	0.031310	0.101279
12	6	0	4.106149	1.373120	0.059051
13	6	0	2.676905	1.571861	-0.016899
14	6	0	2.023503	2.807297	-0.067041
15	6	0	0.625962	2.990552	-0.079546
16	6	0	-0.015566	4.268806	-0.172270
17	6	0	-1.365003	4.061511	-0.136901
18	6	0	-1.592833	2.652833	-0.024277
19	6	0	-2.861873	2.033476	0.009274
20	6	0	-2.994928	0.640927	-0.010636
21	6	0	-1.970029	-0.329047	-0.020307
22	6	0	-2.910521	-4.065562	-0.076530
23	6	0	-3.793501	-4.328550	0.983451
24	6	0	-4.627014	-5.447093	0.954754
25	6	0	-4.594640	-6.319617	-0.134636
26	6	0	-3.723505	-6.066763	-1.195947
27	6	0	-2.888127	-4.949698	-1.167503
28	6	0	4.038599	-2.889731	0.138457

29	6	0	4.402899	-3.516205	1.339767
30	6	0	5.532495	-4.333624	1.401860
31	6	0	6.314998	-4.536427	0.263328
32	6	0	5.962135	-3.917503	-0.937305
33	6	0	4.832105	-3.100240	-0.999090
34	6	0	2.880816	4.037220	-0.104923
35	6	0	3.624174	4.354248	-1.252083
36	6	0	4.429926	5.493516	-1.286214
37	6	0	4.505461	6.332738	-0.173183
38	6	0	3.770570	6.026933	0.974095
39	6	0	2.964307	4.888451	1.007742
40	6	0	-4.076753	2.896097	0.062338
41	6	0	-5.081329	2.787887	-0.912957
42	6	0	-6.210004	3.603304	-0.862208
43	6	0	-6.364118	4.532368	0.169361
44	6	0	-5.379815	4.639765	1.152480
45	6	0	-4.244597	3.830139	1.097895
46	1	0	-4.851460	-1.980564	-0.078749
47	1	0	-0.456844	-5.259068	0.007604
48	1	0	2.183833	-4.777295	0.063840
49	1	0	5.278393	-0.480739	0.167145
50	1	0	4.837101	2.167328	0.085493
51	1	0	0.505288	5.209378	-0.264345
52	1	0	-2.146967	4.802286	-0.201924
53	1	0	-3.815818	-3.655419	1.835402
54	1	0	-5.299618	-5.637685	1.786200
55	1	0	-5.244910	-7.189329	-0.157235
56	1	0	-3.697393	-6.736249	-2.051100
57	1	0	-2.219320	-4.749513	-1.999389
58	1	0	3.796051	-3.356936	2.226540
59	1	0	5.802308	-4.809227	2.340565
60	1	0	7.194159	-5.172527	0.311634
61	1	0	6.564515	-4.072160	-1.828045
62	1	0	4.556636	-2.621167	-1.934324
63	1	0	3.563337	3.703877	-2.119942
64	1	0	4.995594	5.726295	-2.183986
65	1	0	5.132637	7.219198	-0.199468
66	1	0	3.827087	6.672724	1.845819
67	1	0	2.395759	4.650065	1.902018
68	1	0	-4.971684	2.057964	-1.706662
69	1	0	-6.973540	3.510344	-1.629392
70	1	0	-7.247250	5.163831	0.208859
71	1	0	-5.495140	5.350184	1.966352
72	1	0	-3.486465	3.908556	1.871431
73	7	0	-4.272304	0.021572	-0.021897
74	7	0	0.320214	-2.031512	-0.004501
75	7	0	2.063829	0.340372	-0.013213
76	7	0	-0.360540	2.016691	-0.004939

References

1 Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
2 A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.
3 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.
4 P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker and P. D. W. Boyd, *J. Chem. Phys.*, 1989, **91**, 1762.