Supporting Information

Effect of the dangling aromatic ring on neutral luminescent bis(phosphine) Cu(I)/Ag(I) complexes with the asymmetric pyridyl-tetrazolate ligands

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Experimental section

Physical Measurements and Instrumentation. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AV300 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (Me$_4$Si). Elemental analysis was performed on an ElementarVario MICRO Cube elemental analyzer. IR spectra of the solid samples as KBr discs were obtained within the range 4000–400 cm^{-1} on an AVATAR 360 FTIR spectrometer. All of the electronic absorption spectra were recorded on a Hewlett–Packard 8453 or Hewlett– Packard 8452A diode-array spectrophotometer. Steady-state emission spectra were measured at room temperature and at 77 K on a Horiba JobinYvon Fluorolog-3-TCSPC spectrofluorometer. The solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with not less than four successive freeze– pump–thaw cycles. The measurements at 77 K were carried out on dilute solutions of the samples in EtOH/MeOH (4:1, v/v) loaded in a quartz tube inside a quartz-walled Dewar flask that contained liquid nitrogen. Luminescence lifetimes were measured by using the time-correlated single-photon-counting (TCSPC) technique on a Fluorolog-3-TCSPC spectrofluorometer in a fast MCS mode with a Nano LED-375 LH excitation source, which had a peak excitation wavelength at 375 nm and a pulse width of less than 750 ps. The photon-counting data were analyzed on Horiba JobinYvon Decay Analysis Software.

X-ray Crystallography. The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromated Cu K\a radiation (λ = 1.5418 Å). The structures were solved by using the SHELXT-2014 program.[1] The Cu metal atoms and many of the non-hydrogen atoms were located according to the Intrinsic Phasing method. The positions of the other non-hydrogen atoms were located after refinement by full matrix least-squares by using the SHELXL-2018 program.[2] In the final stage of the least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by SHELXL-2018 program. The positions of H atoms were calculated based on riding model with thermal parameters that were 1.2 times that of the associated C atoms and participated in the calculation of the final R indices. The structural analysis was performed using Olex 2.[3] Crystallographic data (including structure factors) of the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre (CCDC) with the depository numbers CCDC 2178439-2178440 for **2** and **7**, respectively.

Computational Details.

All the calculations were done by GAUSSIAN 09, version B.01.[4] The ground state and lowest triplet state structures of complexes **2** and **7** were optimized using B3LYP functional[5] and a mixed basis set of 6-31+G(d) (for C, H, N, P) and LANL2DZ[6] (for Cu). To reduce computation complexity, the phenyl rings of PPh$_3$ ligand is replaced by methyl groups. Polarized Continuum Model[7] (PCM) was employed to account for the solvent effect. Frequency calculations were done after optimization and no imaginary frequencies were found. The X-ray crystal structures of the complexes were used without further optimization.

References:

[1] G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallographica Section A*, 2015, **71**, 3-8.

[2] G. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallographica Section C*, 2015, **71**, 3-8.

[3] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H., *J. Appl. Cryst.* 2009*, **42**, 339-341.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Gaussian 09*, Revision B.01, Gaussian, Inc., Wallingford

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[5] (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652; (b) C. Lee, W, Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem*. 1994, **98**, 11623 – 11627

[6] (a) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241; (b) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys*. 1992, **97**, 2571–2577; (c) W. R. Wadt and P. J. Hay, *J. Chem. Phys*. 1985, **82**, 284–298.

[7] G. Scalmani and M. J. Frisch, *J. Chem. Phys.* 2010, **132**, 114110.
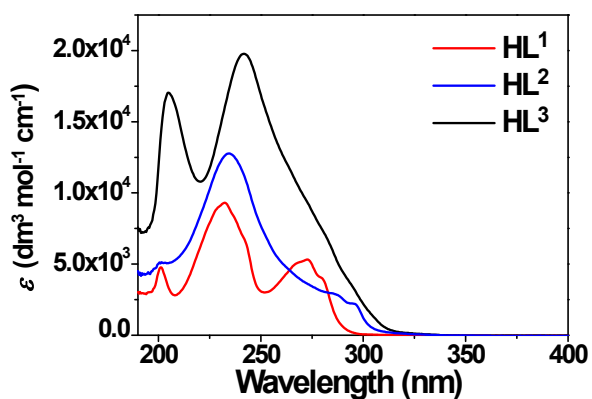
Fig. S1 The UV/vis spectra of HL[1]-HL[3] in MeOH solution.
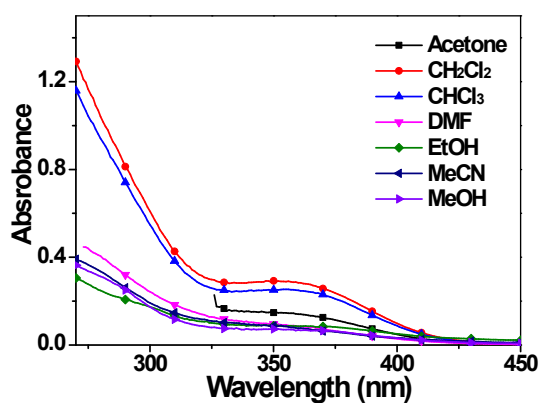
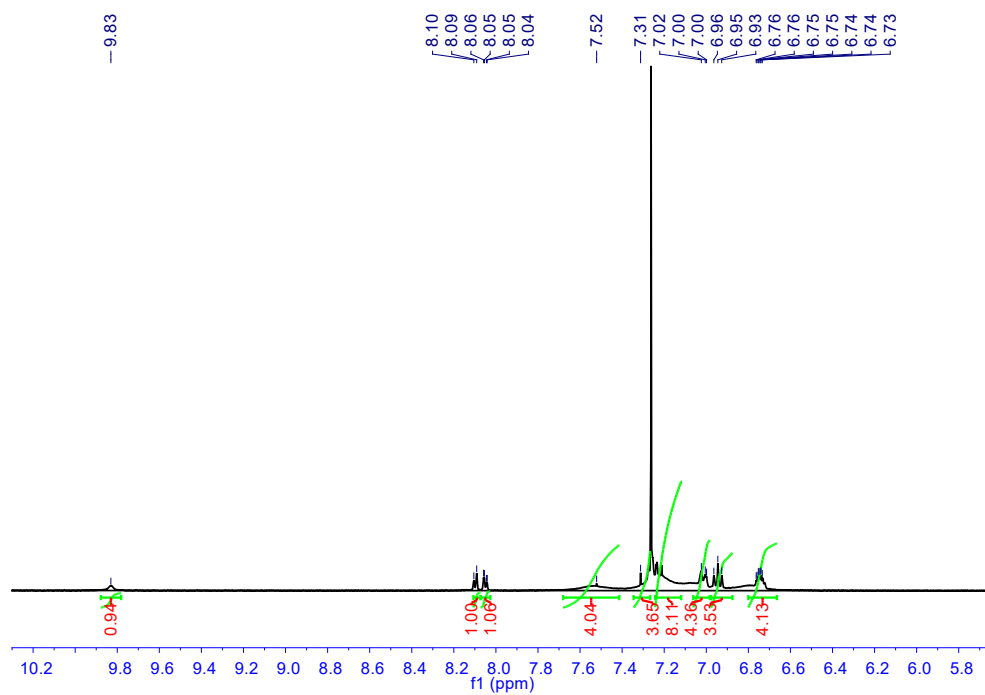**Fig. S2** The absorption spectra of **1** in various solvents.
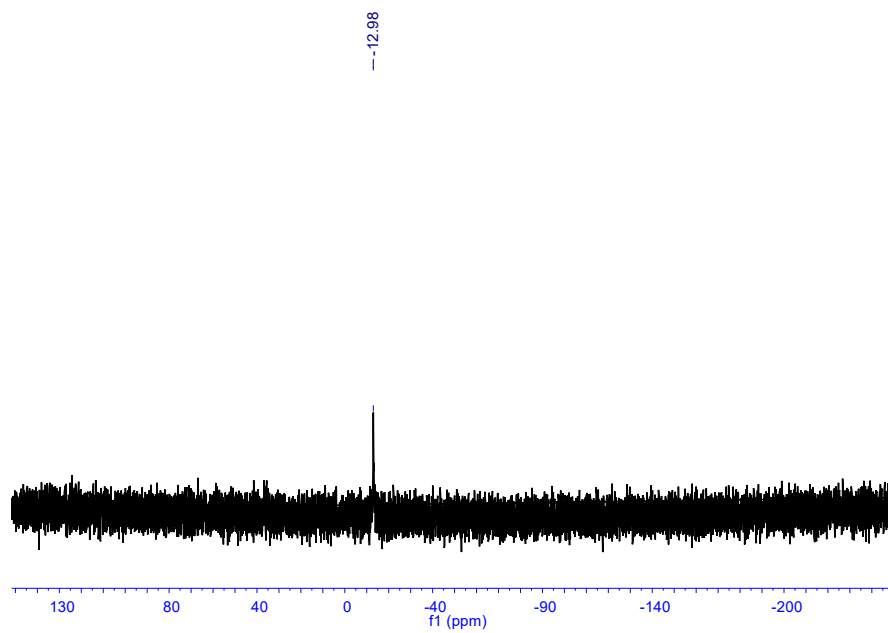
Fig. S3 ^{1}H NMR of **5** in CDCl$_3$.

Fig. S4 ^{31}P{^{1}H} NMR of **5** in CDCl$_3$.
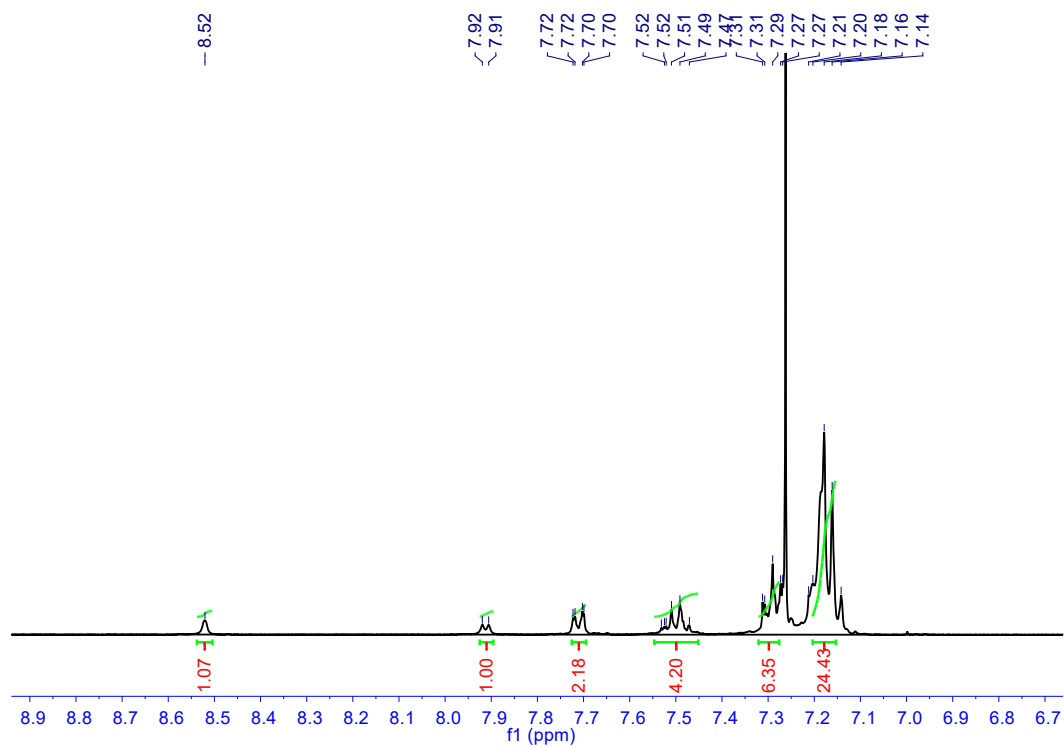
Fig. S5 ^{1}H NMR of **6** in CDCl$_3$.
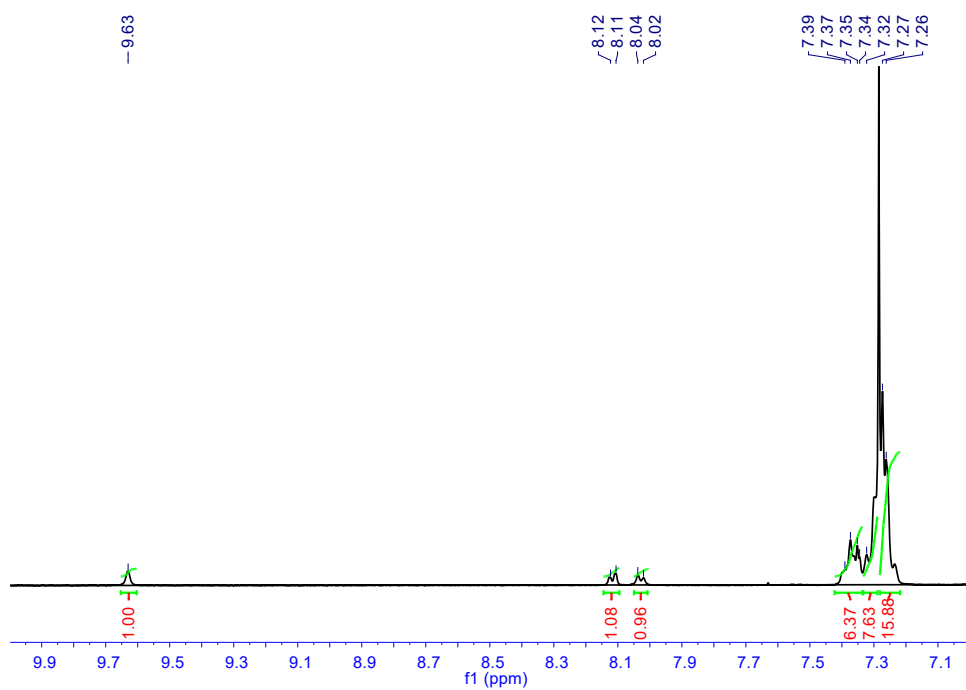
Fig. S6 ^{1}H NMR of **7** in CDCl$_3$.
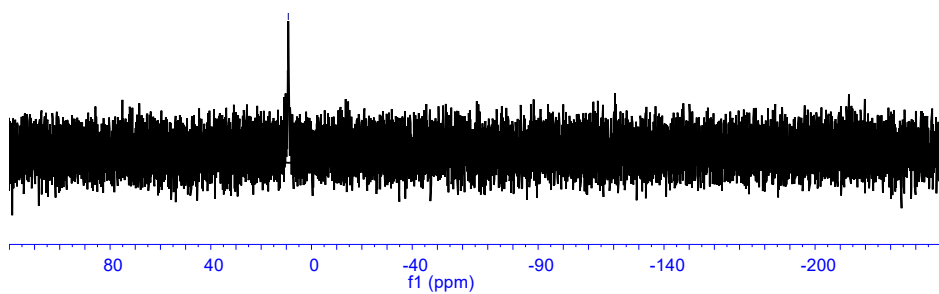
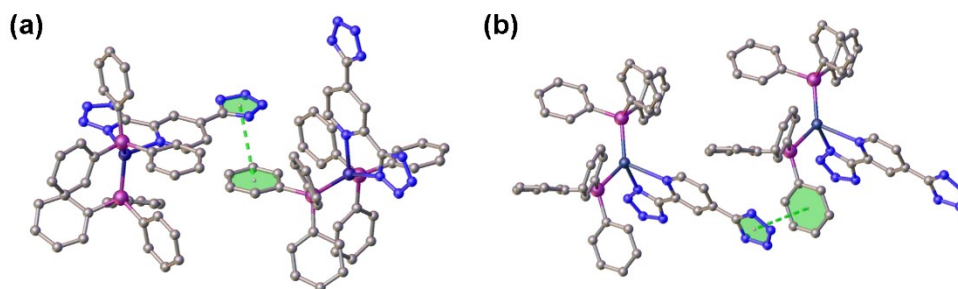**Fig. S7** $^{31}P\{^1H\}$ NMR of **7** in CDCl$_3$.

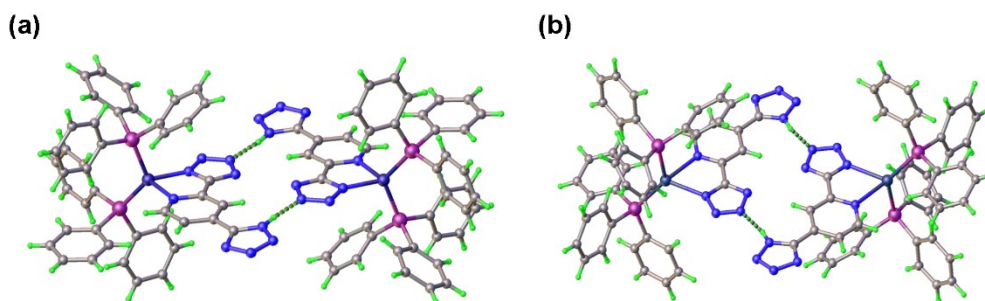**Fig. S8** The π···π stacking interactions in **2**(a), **7**(b).

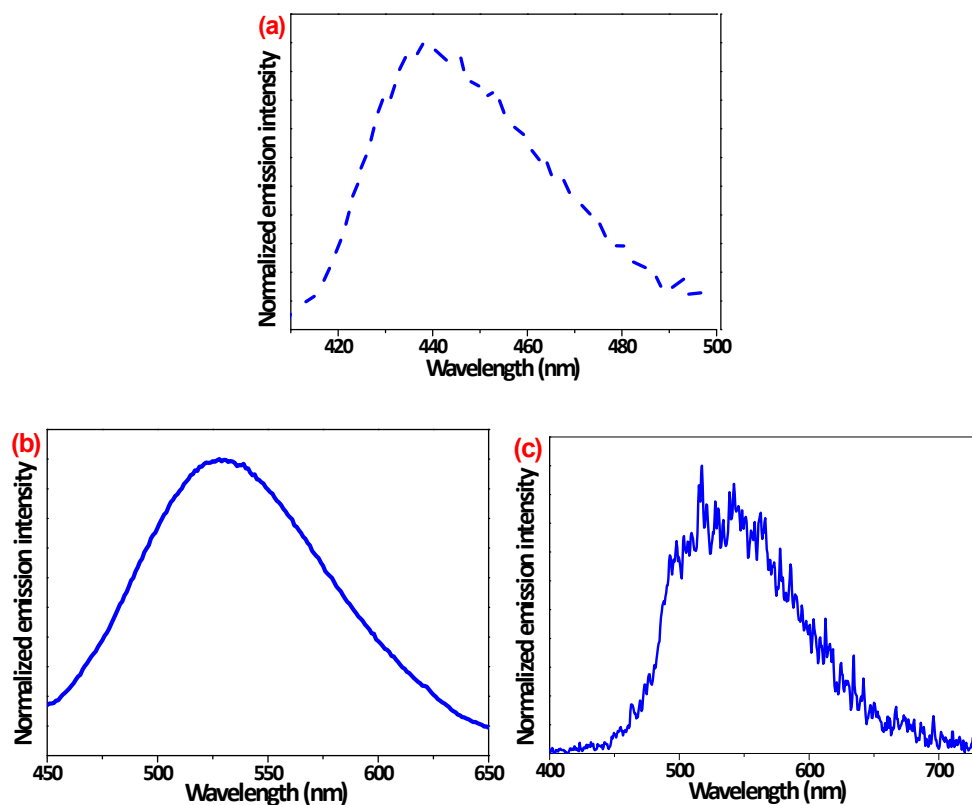**Fig. S9** The Intermolecular H-bonding interactions in **2**(a) and **7**(b).

Fig. S10 Emission spectra of **7** (a) in the CH_2Cl_2 at room temperature. (b) in solid state at room temperature. (c) in low-temperature 77 K glassy media EtOH-MeOH (4:1, v/v) (λ_{ex} = 380 nm).

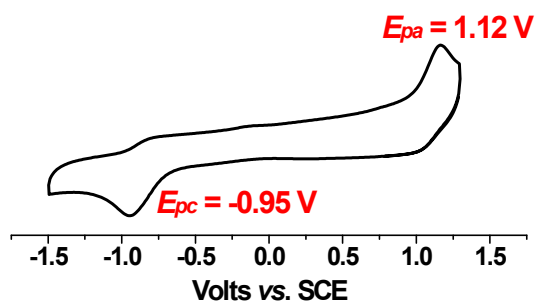**Fig. S11** The CV of **2** in CH_2Cl_2 containing 0.1 M [$^nBu_4N$]PF_6 with scan rate = 0.1 V/s.

Table S1 Summarized CVs data for compounds **1-6** in CH_2Cl_2.

	E_{pa} (ox)	E_{pc} (red)
1	1.06	-1.18
2	1.12	-0.95
3	1.13	-1.48
4	1.12	-1.10
5	1.05	-1.08
6	1.02	-1.02

Table S2 Crystal data and structure refinement details for compounds **2** and **7**.

	2	**7**
Formula	$C_{43}H_{34}CuN_9P_2$	$C_{43}H_{34}AgN_9P_2$
Mr	802.30	846.60
T /K	150.0 (1)	100.0 (1)
Crystal syst	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	18.9696 (2)	19.2853 (9)
b/Å	10.5128 (1)	10.8239 (4)
c/Å	19.2832 (2)	19.3211 (8)
α, (°)	90	90
β, (°)	89.9860 (10)	92.111 (4)
γ, (°)	90	90
V/ Å^3	3845.53 (7)	4030.4 (3)
Z	4	4
ρ_{calcd}, Mg m^{-3}	1.353	1.395
F(000)	1615	1728
Collected refl.	41771	26014
Unique refl.	7724	7814
R(int)	0.060	0.085
R_1, $I > 2\sigma(I)$	0.077	0.066
wR(all)	0.227	0.210
GOF	1.07	1.03
No.of par.	500	484