Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Four highly efficient cuprous complexes and their applications in solution-processed organic light-emitting diodes

Qing Zhang,[a, b, c] Xu-Lin Chen,[a, b] Jun Chen,[c] Xiao-Yuan Wu,[a, b] Rongmin Yu,[a, b] and Can-Zhong Lu*[, a, b]

[a] Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences; Fuzhou, Fujian 350002, China. Fax: +86-591-8370-5794. E-mail: czlu@fjirsm.ac.cn.

[b] Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

[c] Graduate University of Chinese Academy of Sciences, Beijing 100049, China.

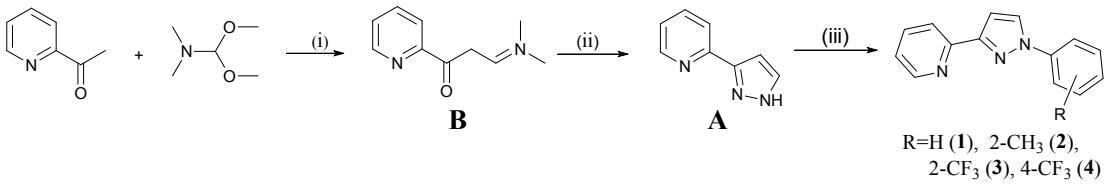

Fig. S1. Synthesis of N-functionalized 3-C-linked pyrazolyl pyridine diimine ligands. (i) Reflux, 16 h. (ii) 2 eq of hydrazine hydrate in ethanol, reflux for 2 h. (iii) 0.2 eq of cuprous iodine, 0.4 eq of 1,10-phenanthroline, 1 eq of benzene halide and 2 eq of cesium carbonate, under nitrogen, at 100 ºC, 24 h.

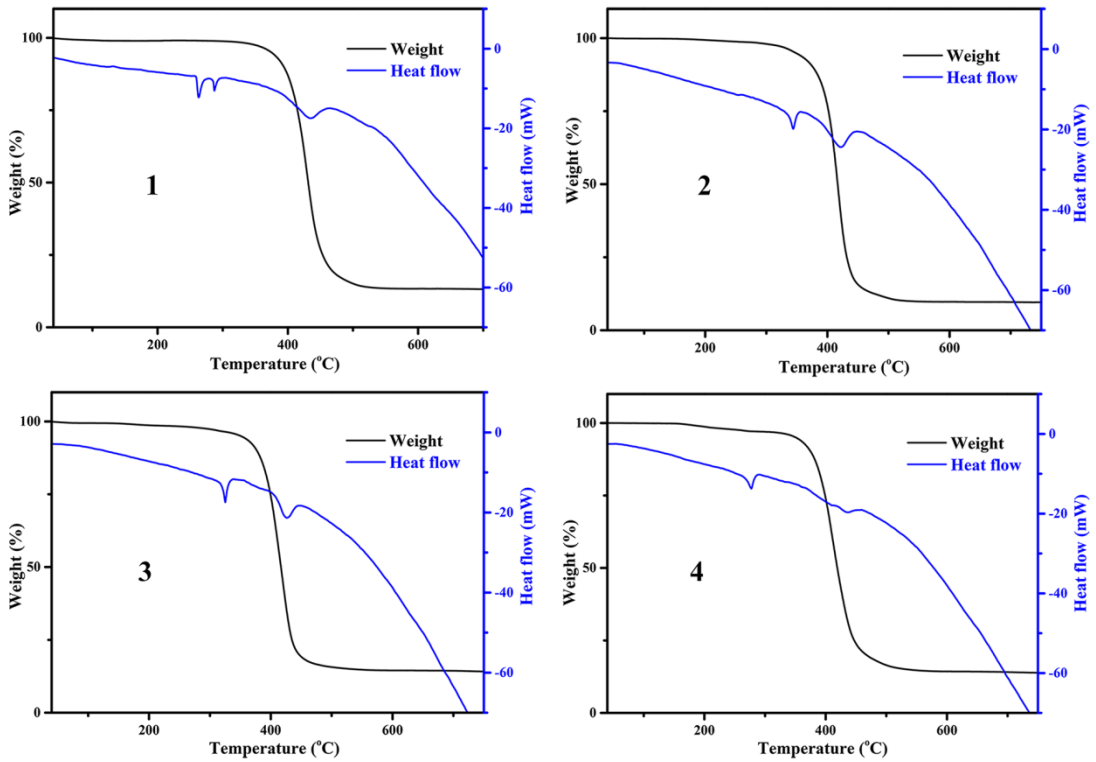

Fig. S2. TGA-plots and heat flow curve of complexes **1**, **2, 3** and **4**.

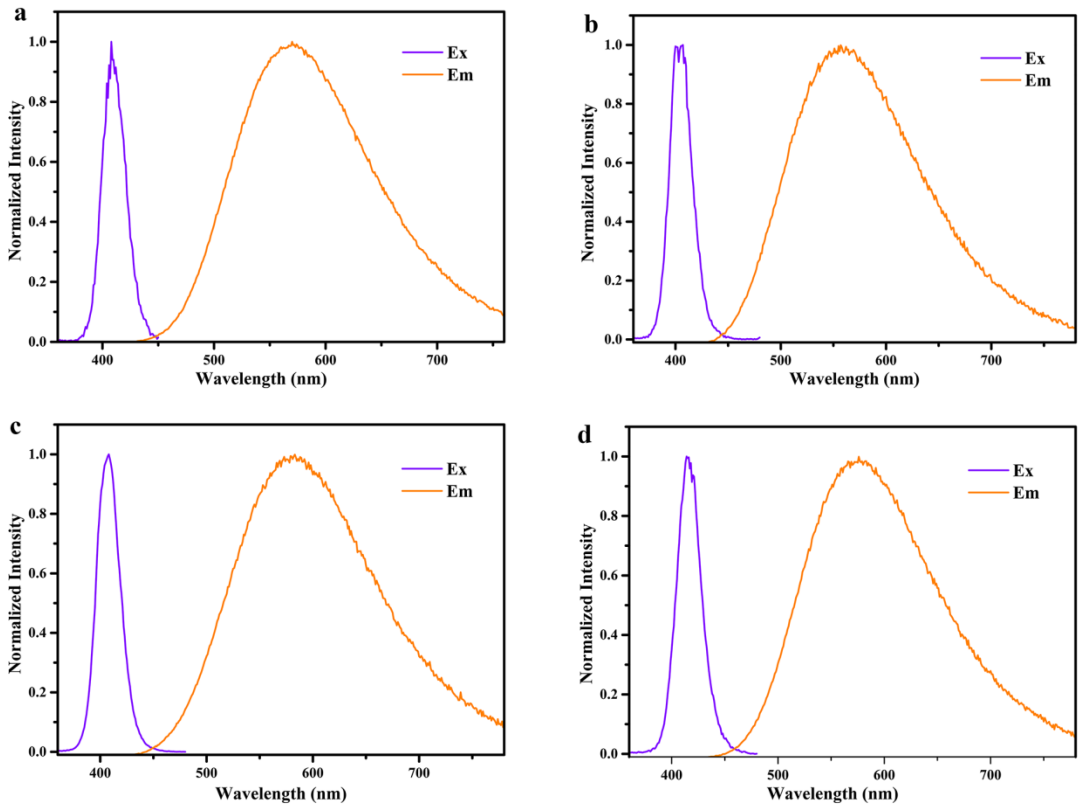

Fig. S3. Excitation and emission spectra of **1** (**a**), **2** (**b**), **3** (**c**) and **4** (**d**) in the degassed CH_2Cl_2.

Table S1. Crystallographic data and structural refinements of **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{52}H_{41}BCl_4CuF_4N_3OP_2$	$C_{51}H_{41}BCuF_4N_3OP_2$	$C_{53}H_{44}BCuF_7N_3O_2P_2$	$C_{51}H_{38}BCuF_7N_3OP_2$
M_r **(g mol^{-1})**	1077.97	924.16	1024.20	978.13
Space group	P-1	C2/c	C2/c	P-1
a**/Å**	13.2091(6)	22.372(5)	22.0434(4)	9.897(3)
b**/Å**	13.3548(7)	19.795(4)	20.1776(3)	13.698(4)
c**/Å**	16.3937(9)	21.048(5)	20.7778(3)	18.292(5)
α**/°**	70.325(5)	90	90	90.898(3)
β**/°**	72.633(4)	97.376(4)	93.697(2)	90.739(2)
γ**/°**	64.418(4)	90	90	108.964(5)
V**/Å^3**	2415.9(2)	9244(4)	9222.4(3)	2344.6(11)
Z	2	8	8	2
D_c**/g cm^{-3}**	1.482	1.328	1.475	1.386
μ**/mm^{-1}**	3.787	0.599	1.967	0.603
F**(000)**	1100	3808	4208	1000
total reflns	15986	36465	16539	22587
unique reflns	9468	10543	9074	10594
R_{int}	0.0290	0.0268	0.0145	0.0312
GOF	1.024	1.078	0.994	1.001
R_1 [a] **[I >2σ(I)]**	0.0534	0.0651	0.0404	0.0606
wR_2 [b] **(all data)**	0.2040	0.2128	0.1270	0.2075
CCDC	1041001	1041002	1041003	1041004

[a] $R_1 = \sum(F_o - F_c) / \sum F_o$; [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) for **1**–**4**.

1			
Cu(1)–N(2)	2.0908(17)	Cu(1)–P(1)	2.2512(6)
Cu(1)–N(3)	2.1102(18)	Cu(1)–P(2)	2.2609(5)
N(2)–Cu(1)–N(3)	79.02(7)	N(2)–Cu(1)–P(2)	106.27(5)
N(2)–Cu(1)–P(1)	135.58(5)	N(3)–Cu(1)–P(2)	116.70(5)
N(3)–Cu(1)–P(1)	107.30(5)	P(1)–Cu(1)–P(2)	109.05(2)
2			
Cu(1)–N(2)	2.095(3)	Cu(1)–P(1)	2.2536(9)
Cu(1)–N(3)	2.106(3)	Cu(1)–P(2)	2.2573(9)
N(2)–Cu(1)–N(3)	79.34(10)	N(2)–Cu(1)–P(2)	112.08(7)
N(2)–Cu(1)–P(1)	128.08(7)	N(3)–Cu(1)–P(2)	112.31(7)
N(3)–Cu(1)–P(1)	107.86(8)	P(1)–Cu(1)–P(2)	111.74(3)
3			
Cu(1)–N(2)	2.0700(17)	Cu(1)–P(2)	2.2410(5)
Cu(1)–N(3)	2.0986(16)	Cu(1)–P(1)	2.2547(5)
N(2)–Cu(1)–N(3)	79.08(7)	N(2)–Cu(1)–P(1)	126.11(5)
N(2)–Cu(1)–P(2)	114.33(5)	N(3)–Cu(1)–P(1)	105.77(5)
N(3)–Cu(1)–P(2)	114.08(5)	P(2)–Cu(1)–P(1)	111.880(19)
4			
Cu(1)–N(3)	2.067(3)	Cu(1)–P(2)	2.2871(10)
Cu(1)–N(2)	2.208(3)	Cu(1)–P(1)	2.3012(10)
N(3)–Cu(1)–N(2)	78.46(10)	N(3)–Cu(1)–P(1)	114.72(8)
N(3)–Cu(1)–P(2)	117.06(8)	N(2)–Cu(1)–P(1)	108.67(8)
N(2)–Cu(1)–P(2)	117.90(7)	P(2)–Cu(1)–P(1)	114.85(3)

Table S3. Decay time of **1** at varied temperatures.

T (K)	77	100	130	150	180	210	250	270	298
τ [a] (μs)	292	286	273	248	200	136	76	50	41

[a] Emission decay time (monoexponential fit, error ± 5%)