Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting information

AIE macrocyclic molecule-based assembled materials with opposite solvent-responsive properties

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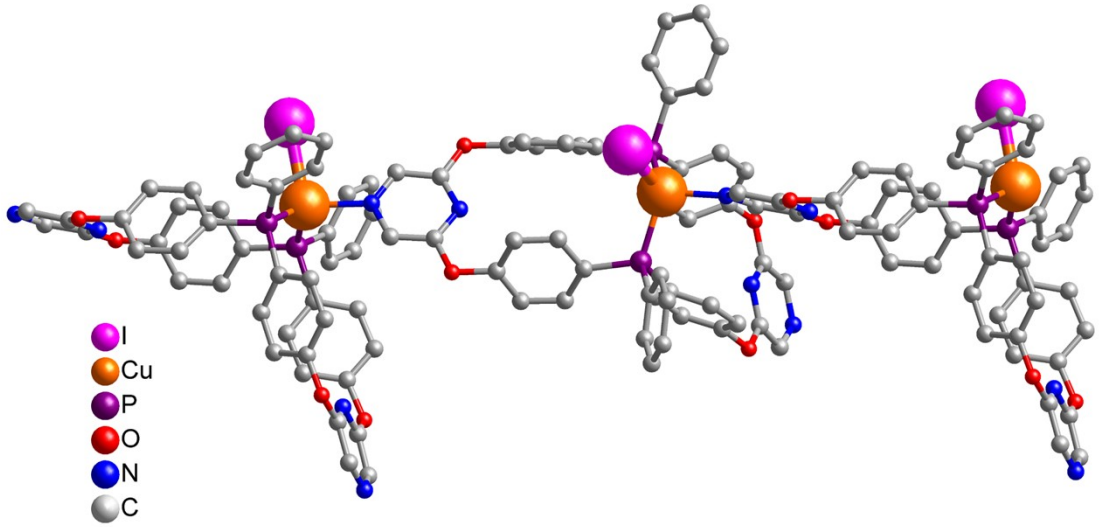

Figure S1. Coordination mode of CuI in **1-EtOH**. The observed bond lengths of Cu-I, Cu-N and Cu-P are 2.6512, 2.118 and 2.2852-2.2974Å respectively (Table S7).

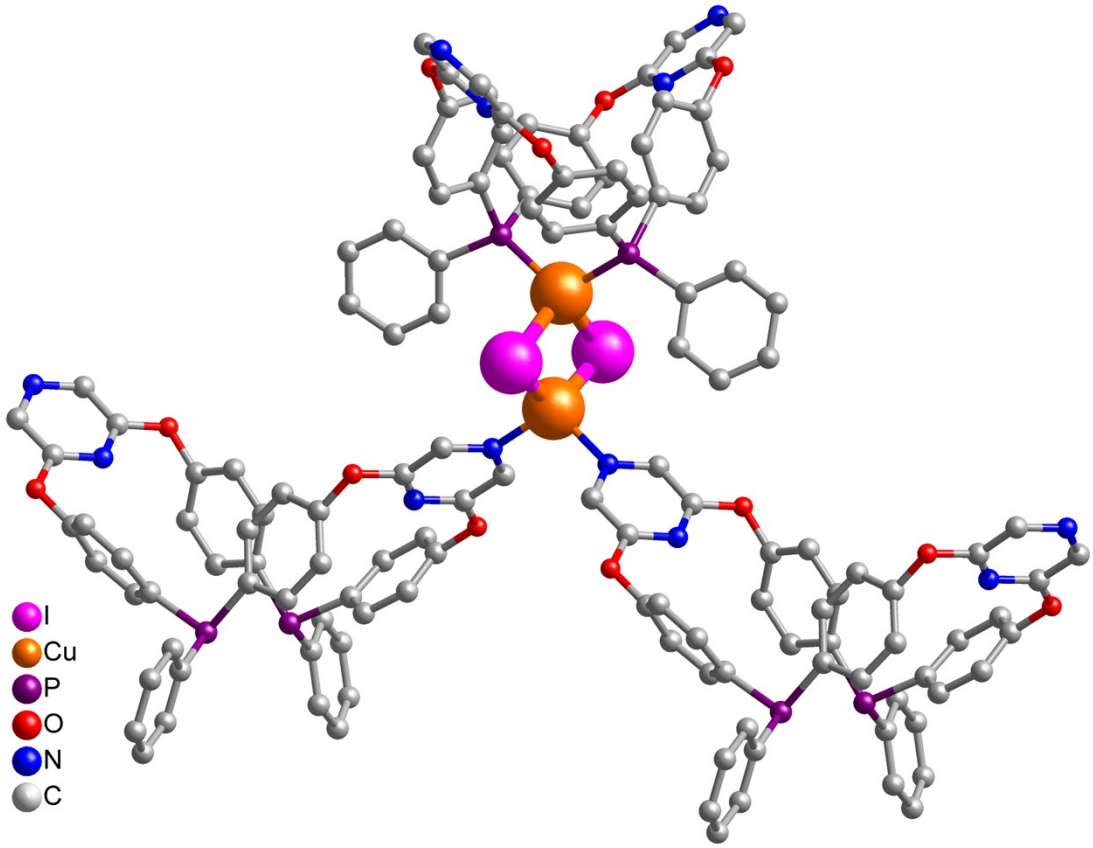

Figure S2. Coordination mode of Cu_2I_2 in **2-EtOH**. The observed bond lengths of Cu-Cu, Cu-I, Cu-N and Cu-P are 2.863, 2.5670-2.7469, 2.084 and 2.3011Å respectively (Table S8).

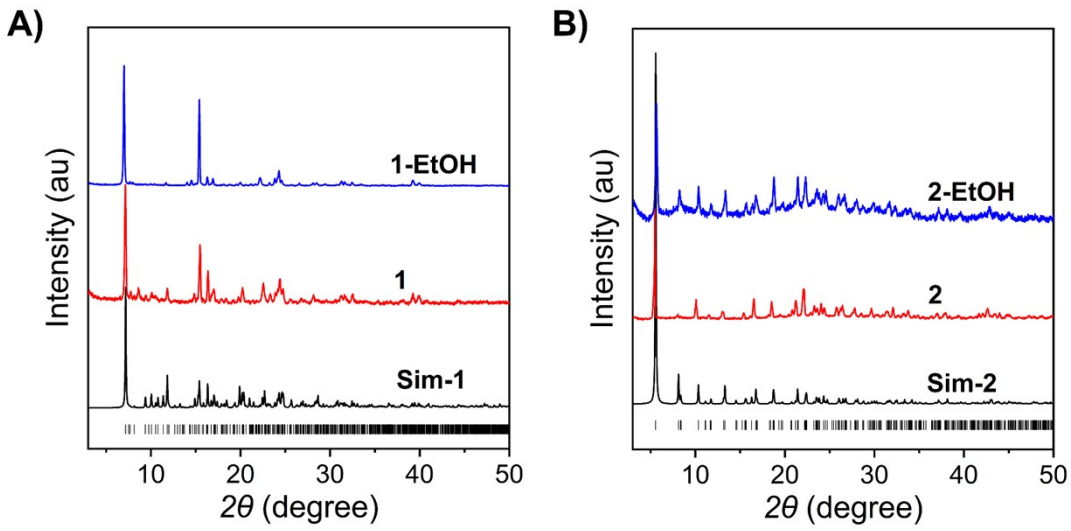

Figure S3. PXRD patterns of **1**/**1-EtOH** (A) and **2**/**2-EtOH** (B).

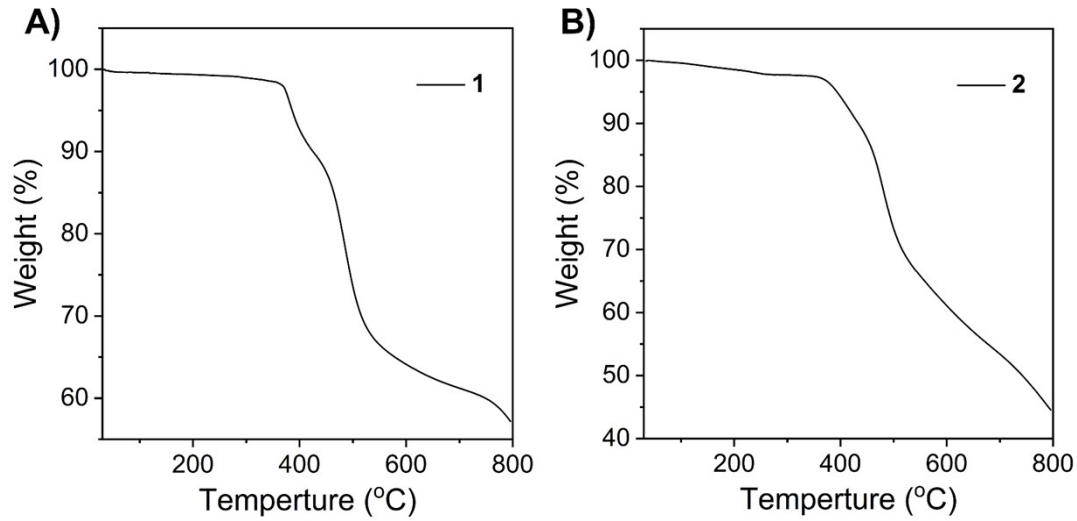

Figure S4. The TGA curves of **1** (A) and **2** (B).

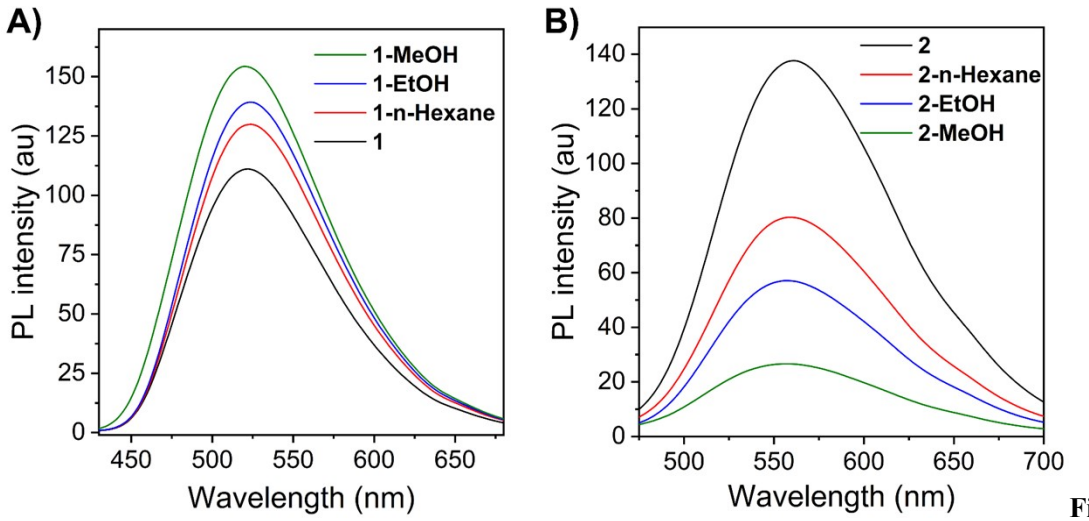

Figure S5. Fluorescence changes of **1** (A) and **2** (B) after fumigation with different solvents.

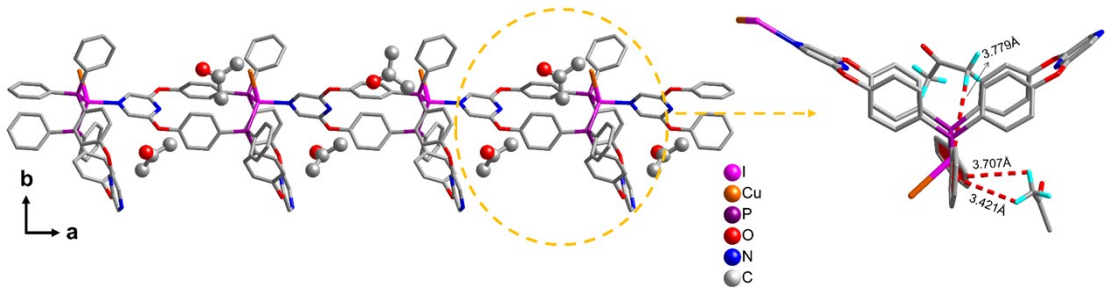

Figure S6. Crystal structure of **1-AC**. There are three types of weak interactions of C-H···π in the structure, with bond lengths of 3.421 Å, 3.707 Å and 3.779 Å, respectively. The main bond lengths (Å) are shown in **Table S5**.

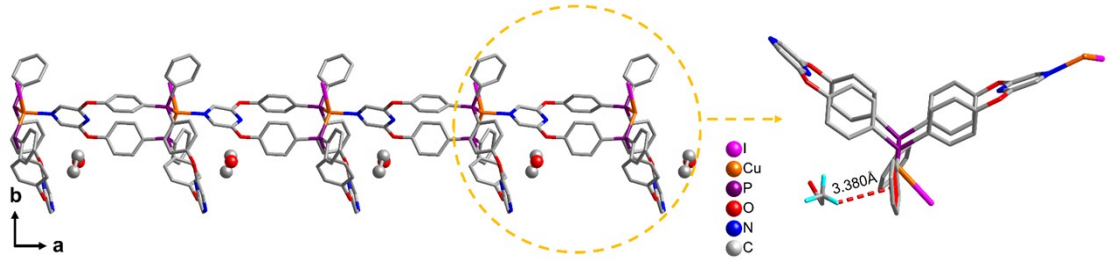

Figure S7. Crystal structure of **1-EtOH**. There is a type of weak interactions of C-H···π in the structure, with bond lengths of 3.380 Å.

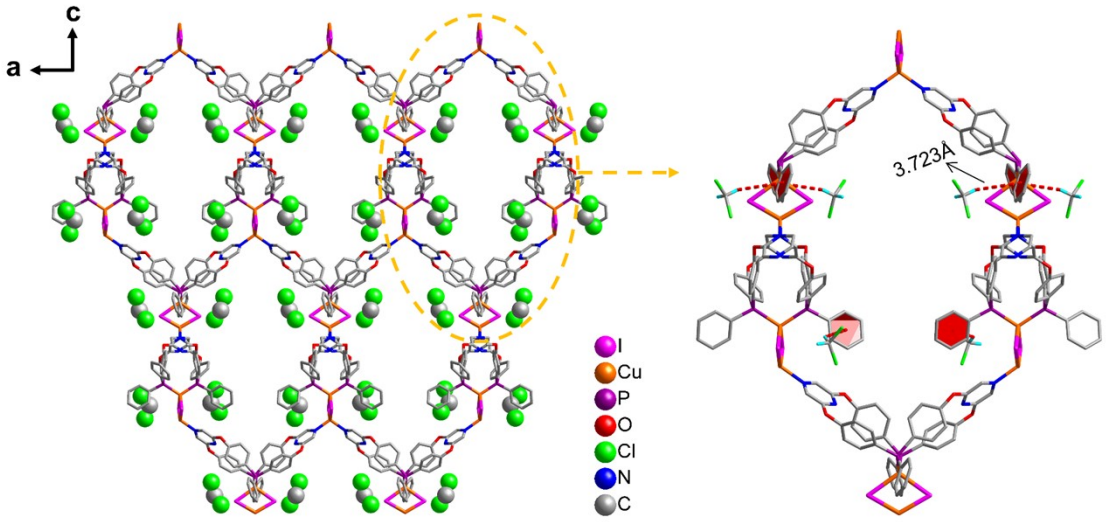

Figure S8. Crystal structure of **2-DCM**. There is a type of weak interactions of C-H···π in the structure, with bond lengths of 3.723 Å. The main bond lengths (Å) are shown in **Table S6**.

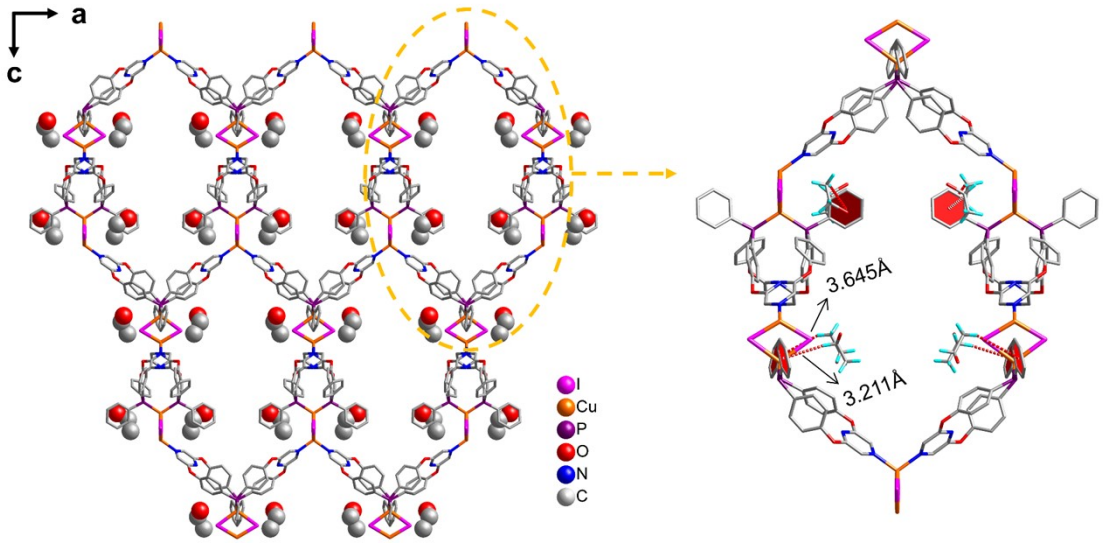

Figure S9. Crystal structure of **2-EtOH**. There are two types of weak interactions of C-H···π in the structure, with bond lengths of 3.211 Å and 3.645 Å.

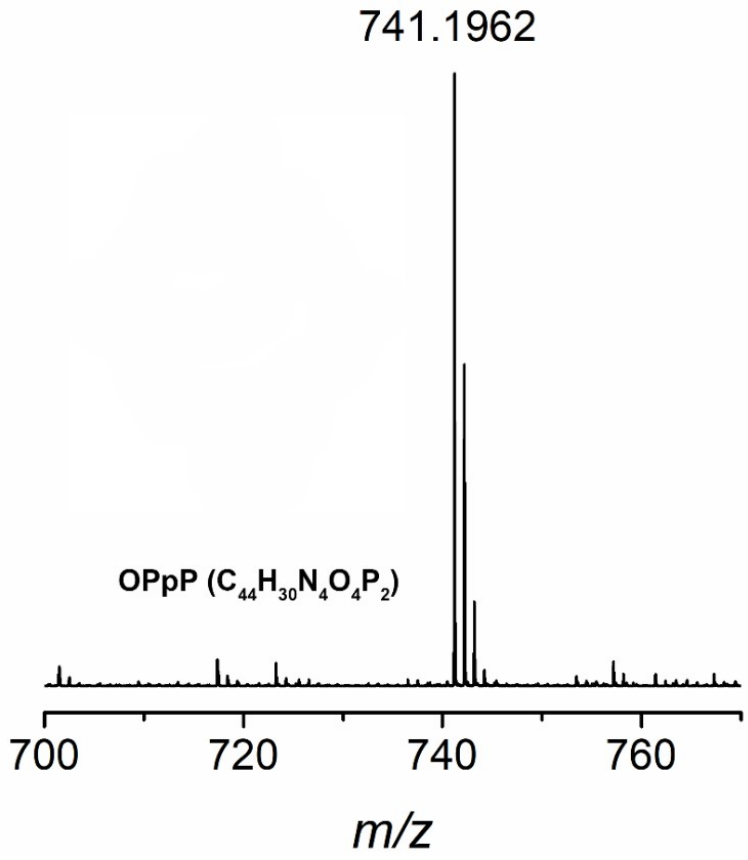

Figure S10. The positive-ion mode ESI-MS spectra of **OPpP**.

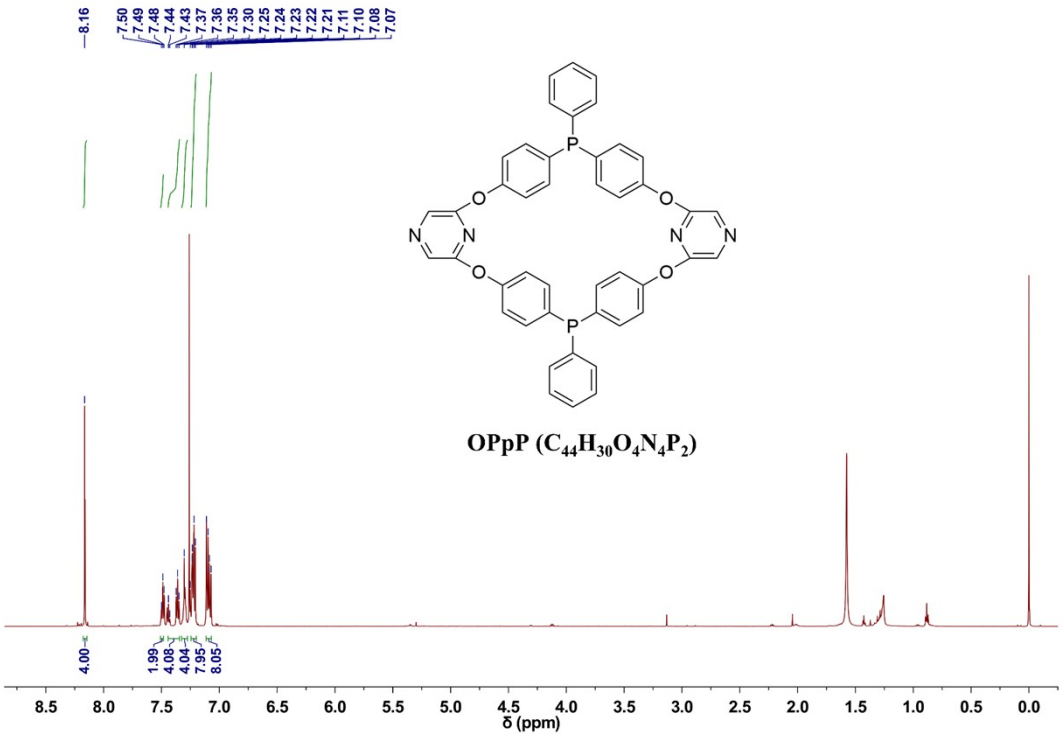

Figure S11. ^{1}H-NMR spectrum of **OPpP**.

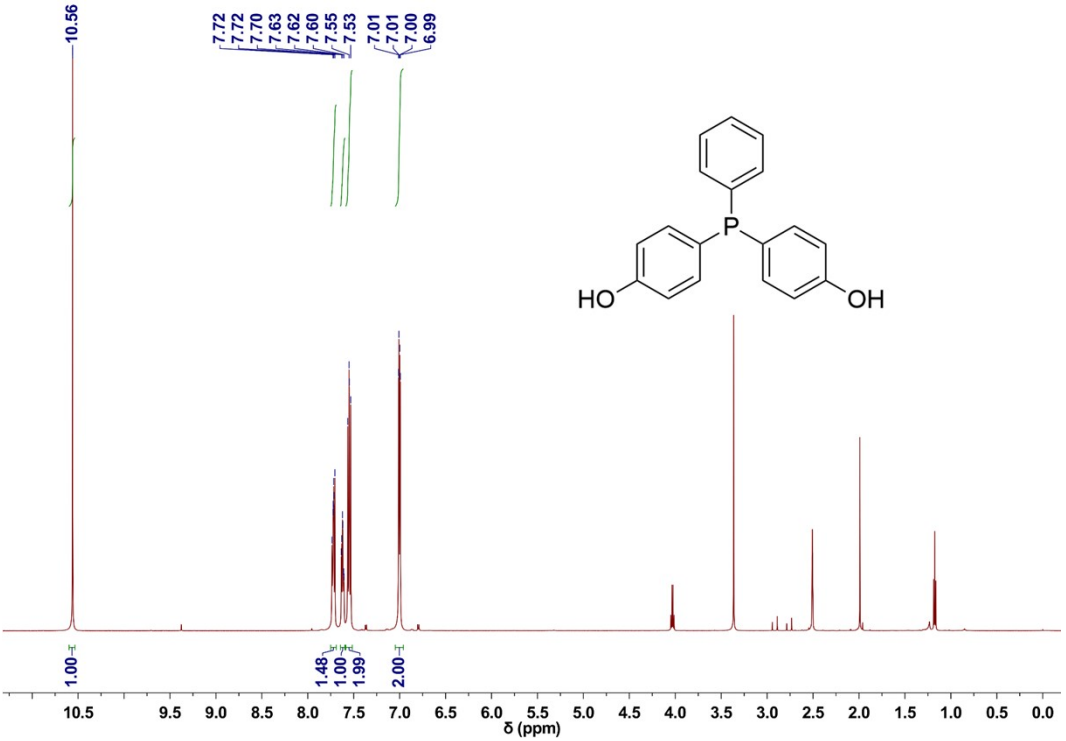

Figure S12. ^{1}H-NMR spectrum of bis(4-hydroxyphenyl) phenylphosphine.

Table S1. Crystal data and structure refinements of **OPpP**.

	OPpP
Empirical formula	$C_{47}H_{36}N_4O_5P_2$
Formula weight	798.74
Temperature/K	200.00(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	13.3390(2)
b/Å	13.8841(2)
c/Å	14.0251(3)
α/°	119.418(2)
β/°	99.010(2)
γ/°	102.726(2)
Volume/Å^3	2097.03(8)
Z	2
ρ_{calc} g/cm^3	1.265
μ/mm^{-1}	1.356
F (000)	832.0
Crystal size/mm^3	0.08 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.15 to 147.504
Index ranges	$-16 \le h \le 15$, $-17 \le k \le 17$, $-16 \le l \le 17$
Reflections collected	20675
Independent reflections	8157 [R_{int} = 0.0418, R_{sigma} = 0.0522]
Data/restraints/parameters	8157/17/527
Goodness-of-fit on F^2	1.092
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0931, wR_2 = 0.2603
Final *R* indexes [all data]	R_1 = 0.1138, wR_2 = 0.2705
Largest diff. peak/hole / e Å^{-3}	0.95/-0.49
CCDC	2263667

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

Table S2. Crystal data and structure refinements of **1-AC** and **2-DCM**.

	1-AC	**2-DCM**
Empirical formula	$C_{50}H_{42}CuIN_4O_6P_2$	$C_{46.5}H_{35}Cl_5Cu_2I_2N_4O_4P_2$
Formula weight	1047.25	1333.85
Temperature/K	200.00(10)	200.00(10)
Crystal system	orthorhombic	tetragonal
Space group	*Pbca*	$I4_1/a$
a/Å	22.9849(2)	17.1153(5)
b/Å	16.3986(2)	17.1153(5)
c/Å	24.5553(2)	42.312(4)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	9255.39(16)	12394.7(14)
Z	8	8
ρ_{calc} g/cm^3	1.503	1.430
μ/mm^{-1}	6.999	11.451
F (000)	4240.0	5224.0
Crystal size/mm^3	0.2 × 0.05 × 0.02	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.538 to 148.716	8.122 to 147.478
Index ranges	$-28 \le h \le 23$, $-14 \le k \le 20$, $-30 \le l \le 29$	$-15 \le h \le 20$, $-20 \le k \le 20$, $-51 \le l \le 52$
Reflections collected	34052	15882
Independent reflections	9212 [R_{int} = 0.0351, R_{sigma} = 0.0359]	6019 [R_{int} = 0.0465, R_{sigma} = 0.0517]
Data/restraints/parameters	9212/0/540	6019/42/317
Goodness-of-fit on F^2	1.030	1.050
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1097	R_1 = 0.0650, wR_2 = 0.1779
Final *R* indexes [all data]	R_1 = 0.0515, wR_2 = 0.1148	R_1 = 0.0908, wR_2 = 0.1993
Largest diff. peak/hole / e Å^{-3}	1.09/-0.96	1.64/-0.99
CCDC	2263668	2263670

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

Table S3. Crystal data and structure refinements of **1-EtOH** and **2-EtOH**.

	1-EtOH	**2-EtOH**
Empirical formula	$C_{46}H_{36}CuIN_4O_5P_2$	$C_{54}H_{60}Cu_2I_2N_4O_9P_2$
Formula weight	976.16	1351.88
Temperature/K	200.00(10)	200.00(10)
Crystal system	orthorhombic	tetragonal
Space group	*Pbca*	$I4_1/a$
a/Å	22.9312(3)	16.95920(10)
b/Å	16.4231(2)	16.95920(10)
c/Å	24.9422(4)	43.1583(2)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	9393.3(2)	12412.95(16)
Z	8	8
ρ_{calc} g/cm^3	1.381	1.447
μ/mm^{-1}	6.839	9.566
F (000)	3928.0	5424.0
Crystal size/mm^3	0.05 × 0.03 × 0.02	0.05 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.51 to 149.108	5.598 to 148.762
Index ranges	$-20 \le h \le 28$, $-19 \le k \le 11$, $-26 \le l \le 31$	$-21 \le h \le 21$, $-21 \le k \le 21$, $-40 \le l \le 53$
Reflections collected	34486	70553
Independent reflections	9336 [R_{int} = 0.0521, R_{sigma} = 0.0485]	6293 [R_{int} = 0.0402, R_{sigma} = 0.0158]
Data/restraints/parameters	9336/47/534	6293/18/315
Goodness-of-fit on F^2	1.059	1.082
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1207	R_1 = 0.0363, wR_2 = 0.1020
Final *R* indexes [all data]	R_1 = 0.0568, wR_2 = 0.1263	R_1 = 0.0374, wR_2 = 0.1027
Largest diff. peak/hole / e Å^{-3}	0.60/-1.27	1.09/-0.63
CCDC	2263669	2263671

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

Table S4. The radiative (k_r) and non-radiative (k_{nr}) decay rates of **1**, **1-EtOH**, **2** and **2-EtOH**.

	τ (μs)	QY (%)	k_r (s^{-1})	k_{nr} (s^{-1})
1-EtOH	5.38	68	1.3×10^5	6.0×10^4
1	4.67	54	1.2×10^5	9.9×10^4
2	5.43	11	2.0×10^4	1.6×10^5
2-EtOH	5.68	4.4	8.0×10^3	1.7×10^6
OPpP(aggregate)	7.03×10^{-3}	12	1.7×10^7	1.3×10^8
OPpP (solvent)	2.72×10^{-3}	1.3	4.8×10^6	3.6×10^8

Abbreviation: φ=fluorescence quantum yield, k_r=radiative decay rate constant=φ/τ, k_{nr}=nonradiative decay rate constant=(1-φ)/τ, where τ= luminescence lifetime.

Table S5. The main bond lengths (Å) of **1-AC**.

Atom	Atom	Length/ Å
I1	Cu1	2.6512(5)
Cu1	P1[1]	2.2852(10)
Cu1	P2[1]	2.2974(9)
Cu1	N1	2.118(3)

[1]1/2+X,+Y,1/2-Z

Table S6. The main bond lengths (Å) of **1-EtOH**.

Atom	Atom	Length/ Å
I1	Cu1	2.6767(5)
Cu1	P1[1]	2.2937(10)
Cu1	P2[1]	2.2805(9)
Cu1	N1	2.119(3)

[1]1/2+X,+Y,3/2-Z; [2]-1/2+X,+Y,3/2-Z

Table S7. The main bond lengths (Å) of **2-DCM**.

Atom	Atom	Length/ Å
I1	Cu1[1]	2.7354(10)
I1	Cu2	2.5673(9)
Cu1	Cu2[2]	2.863(2)
Cu1	P1[3]	2.2991(19)
Cu1	P1	2.2991(19)
Cu2	N1	2.094(6)
Cu2	N1[4]	2.095(6)

[1]5/4-Y,-1/4+X,-1/4+Z; [2]3/4-Y,1/4+X,1/4+Z; [3]1-X,3/2-Y,+Z; [4]1-X,1/2-Y,+Z

Table S8. The main bond lengths (Å) of **2-EtOH**.

Atom	Atom	Length/ Å
I1	Cu1[1]	2.7469(4)
I1	Cu2	2.5670(4)
Cu1	Cu2[2]	2.863(2)
Cu1	P1[3]	2.3011(8)
Cu1	P1	2.3011(8)
Cu2	N1	2.084(3)
Cu2	N1[4]	2.084(3)

[1]5/4-Y,3/4+X,-1/4+Z; [2]-3/4+Y,5/4-X,1/4+Z; [3]3/4-Y,1/4+X,1/4+Z; [4]-X,3/2-Y,+Z; [5]1-X,3/2-Y,+Z