Supporting Information

Achieving Dual Emission of Thermally Activated Delayed Fluorescence and Ultralong Room-Temperature Phosphorescence by Controlling Excited States Dynamics through Metal Coordination

Xian-Bao Cai, Dong Liang, Deng-Chao Zhang, Ji-Hui Jia, Xiao-Yuan Wu, and Can-Zhong Lu*

Table of Contents

- 1. General Information
- 2. Synthesis
- 3. Single Crystals Information
- 4. Thermal Properties
- **5. Electrochemical Measurements**
- 6. Theoretical Calculations
- 7. Photophysical Measurements
- 8. NMR, MS, and HPLC spectra
- 9. Reference

1. General Information

All reactions were carried out under the nitrogen atmosphere unless specified. Chemicals were purchased from commercial sources and used without further purification. The solvent were freshly distilled on suitable dry reagents. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECZ400S 400 MHz NMR spectrometer and a JEOL ECZ600R 600 MHz NMR spectrometer. Elemental analyses (C, H, N) were carried out with an Elementar Vario EL III elemental analyzer. TGA and differential scanning calorimetry (DSC) of samples were performed on a METTLER TOLEDO TGA/DSC 1 STARe System with a heating rate of 10 °C/min under nitrogen. UV-visible absorption spectra were determined on a PerkinElmer Lambda 365 spectrophotometer under ambient conditions. PL spectra of solution, film samples were carried out with an Edinburgh FLS1000 fluorescence spectrometer. The transient PL and time-resolved PL characteristics of solution and film samples were performed on an Edinburgh analytical instrument FLS1000 with a xenon arc lamp (450 W), EPL-375 laser and pulsed flash lamps. The PL quantum yields of solution and film samples were defined as the number of photons emitted per photon absorbed by the systems and measured by an Edinburgh FLS1000 spectrofluorophotometer. And the variable-temperature measurements were carried out on corresponding instruments by using an additional LINKAM THMS600 system.

2. Synthesis



Scheme S1 Synthesis route of the Phen-Tpa ligand.

Synthesis of Phen-Tpa. Compound **Phen-Tpa** was prepared according to the reported procedure,¹ To a solution of 3,8-dibromo-1,10-phenanthroline (338 mg, 1.0 eq, 1.0 mmol) dissolved in the toluene (10 mL) under N₂. Then, the [4-(N-phenylanilino)phenyl]boronic acid (635.8 mg, 2.2 eq, 2.2 mmol) in solution in dry THF (10 mL) and potassium carbonate K₂CO₃ (552 mg, 4 eq, 4 mmol) in solution in distilled water (2 mL), are added. Then, tetrakis(triphenylphosphine)palladium(0) (115.6 mg, 5 mol%, 0.1 mmol) is added to the mixture. The reaction mixture was refluxed for 24 h at 110°C in an oil bath. When it is cool, the solvent was removed by vacuum-rotary evaporation. The residue was extracted with CH_2Cl_2 . The extract was dried using anhydrous sodium sulfate. The product as a green solid was obtained by column chromatography on silica gel (533 mg, 80%). ¹H

NMR (400 MHz, DMSO-D6) δ 9.40 (d, J = 1.2 Hz, 2H), 8.71 (d, J = 1.2 Hz, 2H), 8.04 (s, 2H), 7.89 (d, J = 7.6 Hz, 4H), 7.36 (t, J = 7.3 Hz, 8H), 7.15 – 7.09 (m, 16H). ¹³C NMR (151 MHz, DMSO-D6) δ 148.27, 147.70, 146.85, 144.07, 133.91, 132.26, 130.17, 129.72, 128.39, 128.25, 127.30, 124.53, 123.64, 122.95. Anal. Calcd for C₄₈H₃₄N₄: C, 86.46; H, 5.14; N, 8.40. Found: C, 86.01; H, 5.18; N, 8.38.

Synthesis of Complex 1 ([Ag(Phen-Tpa)(Xantphos)]BF₄). A mixture of Phen-Tpa (0.1 mmol) and Xantphos (0.1 mmol) in CH₂Cl₂ (10 ml) was stirred for 30 min at room temperature, and then [Ag(CH₃CN)₄]BF₄ (0.1 mmol) was added. After the mixture was stirred for 1 hour. The product as crystalline solid was obtained from a diffusion of toluene into the above CH₂Cl₂ solution. ¹H NMR (400 MHz, DMSO-D6) δ 8.86 (s, 4H), 8.15 (s, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 5.8 Hz, 4H), 7.38 (t, J = 7.6 Hz, 8H), 7.32 (s, 4H), 7.25 – 7.07 (m, 34H), 6.69 – 6.55 (m, 2H), 1.57 (s, 6H). ¹³C NMR (101 MHz, DMSO-D6) δ 153.02, 148.76, 148.12, 146.65, 135.28, 134.08, 132.99, 132.47, 131.46, 130.98, 130.34, 129.77, 128.92, 128.24, 127.82, 125.16, 124.62, 123.88, 122.69, 35.04, 29.27. Anal. Calcd for C₈₇H₆₆AgBF₄N₄OP₂: C, 72.58; H, 4.58; N, 3.89. Found: C, 71.86; H, 4.59; N, 3.90.

3. Single Crystals Information

X-ray Crystallographic Analysis. Diffraction data for free ligand Phen-Tpa and **1** were collected on a Supernova single-crystal diffractometer equipped with graphite-monochromatized Ga K α radiation (λ =1.34050 Å) at 100 K. Structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXL-97 program package.² Hydrogen atoms were added in idealized positions. All nonhydrogen atoms were refined anisotropically. Details of the crystal and structure refinements are listed in **Table S1**. Selected bond lengths and bond angles are listed in **Table S2**. CCDC 2414838 and 2414839 contain the supplementary crystallographic data for Phen-Tpa and complex **1**, respectively.

Compound reference	1	Phen-Tpa
Chemical formula	$C_{94}H_{74}AgBF_4N_4OP_2$	$C_{55}H_{46}N_4O_{2.25}$
Formula Mass	1532.19	799.00
Temperature/K	100.00(10)	101(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.9145(2)	9.74650(10)
b/Å	15.9498(2)	10.17140(10)
c/Å	19.2708(4)	21.3460(2)
α/°	77.0980(10)	89.8470(10)
β/°	81.031(2)	85.1040(10)
γ/°	77.6880(10)	75.2930(10)
Volume/Å ³	3755.75(11)	2038.95(4)

 Table S1. Selected crystallographic data of free ligand Phen-Tpa and complex 1.

Z		2		2	
ρ _{calc} g	/cm ³	1.355		1.3	01
µ/m	m ⁻¹	2.053		0.4	00
F(00	00)	1584.0		844	.0
Crystal s	ize/mm ³	0.3 × 0.2 × 0.	1	0.5 × 0.2	5 × 0.15
Radia	ation	Ga Kα (λ = 1.34	05)	Ga Kα (λ :	= 1.3405)
Reflections	collected	48504		387	53
Independent	reflections	14788 [R _{int} = 0.043 5, R _{si}	_{gma} = 0.0443]	7974 [R _{int} = 0.0328	8, R _{sigma} = 0.0222]
Data/restraints	s/parameters	14788/0/967	,	7974/0)/579
Goodness-	of-fit on F ²	1.043		1.0	56
Final R indexe	es [I>=2σ (I)]	R ₁ = 0.0339, wR ₂ =	0.0824	R ₁ = 0.0392, v	vR ₂ = 0.0979
Final R index	es [all data]	R ₁ = 0.0433, wR ₂ =	0.0851	R ₁ = 0.0425, v	vR ₂ = 0.1006
Largest diff. pe	ak/hole / e Å ⁻³	0.86/-0.68		0.26/-	0.29

T	<u> </u>			
Table S2.	Selected bond d	listances (A)	and angles () of complex 1

Compound		1
Distances (Å)	Ag-N1	2.3165(15)
	Ag-N2	2.3744(18)
	Ag-P1	2.5132(6)
	Ag-P2	2.3890(6)
Bond Angles (°)	N1-Ag-N2	71.477(57)
	P1-Ag-P2	116.044(21)
	N1-Ag-P1	104.396(46)
	N2-Ag-P2	121.786(43)
Dihedral angles (°)	P-Ag-P	86.2(6)
	N-Ag-N	



Figure S1 The dihedral angles between the donor triphenylamine and the acceptor phenanthroline in Phen-Tpa and **1**.

4. Thermal Properties



Figure S2 Thermogravimetric analysis curves of Phen-Tpa and 1.

5. Electrochemical Measurements

Cyclic voltammetry was performed in a gastight single-compartment three-electrode cell with a CHI840D Voltammetric Analyzer at a sweep rate of 20 mV/s. A glassy carbon disk (6 mm diameter) and a platinum wire were selected as the working and auxiliary electrodes, respectively. The reference electrode was Ag/Ag⁺ (0.01 M of AgNO₃ in acetonitrile). The CV measurements were carried out in anhydrous and nitrogen-0.1 saturated dichloromethane solutions with Μ ntetrabutylammonium hexafluorophosphate and 2.0 mM investigated compounds. Each experiment concluded with the calibration of its potential against the ferricenium/ferrocene couple (Fc/Fc⁺), which served as an internal redox standard, ensuring all potentials were determined relative to Fc.³ For the CV experiments, feedback compensation has been employed to take into account the ohmic drop.⁴ The HOMO and LUMO levels were estimated from the cyclic voltammetry and optical bandgaps (Eg) determined from the onset of the absorption band (λ_{onset}).

HOMO = -[EOX - $E(Fc/Fc^{+}) + 4.8$] eV;

Eg = 1240/ λ_{onset} ;

LUMO = HOMO + Eg.



Figure S3. Cyclic voltammogram of the 1 and free ligand Phen-Tpa in degassed Dichloromethane.

6. Theoretical Calculations

All the calculations were carried out using the Gaussian 09 program package.⁵ The density functional theory (DFT) and time-dependent (TD-DFT) density functional theory calculations were performed at PBE0 level using 6-31g*/LANL2DZ basis sets in conjunction with the polarizable continuum model (PCM). The structure in the singlet ground (S₀) was optimized via DFT. The S₁ and T₁ geometries were optimized via TDDFT. The input coordinates were extracted from the X-ray crystallographic data. The SOC (spin-orbit coupling) calculations were further evaluated using ORCA 5.0 program.⁶⁻¹⁰ The partition orbital compositions were analyzed by the Multiwfn 2.4 program.¹¹

Figure S4 (a) NTO pairs for S₁ and T₁ states of Phen-Tpa, (b) NTO pairs for S₁ and T₁ states of complex 1 in the optimized S₁ and T₁ structure.

Figure S5 Frontier orbitals from HOMO-3 to LUMO+4 of Phen-Tpa in the optimized S_0 structure.

Figure S6 Frontier orbitals from HOMO-3 to LUMO+4 of 1 in the optimized S₀ structure.

Table S3. Composition of HOMO-3 - LUM	D+4 of complex 1 and Phen-T	pa in the optimized S ₀ structure.
---------------------------------------	------------------------------------	---

		Energy (eV)	Ag	Тра	Phen	Xantphos
	HOMO-3	-8.2888	5.45926 %	3.80056 %	4.02322 %	86.71696 %
	HOMO-2	-7.9561	20.87027 %	0.19072 %	2.33916 %	76.59984 %
	HOMO-1	-6.8894	0.02642 %	93.96286 %	5.91249 %	0.09823 %
	НОМО	-6.7600	0.01536 %	93.20238 %	6.75695 %	0.02532 %
1	LUMO	-3.7949	1.45907 %	18.45507 %	78.09098 %	1.99488 %
	LUMO+1	-3.5910	0.09201 %	9.94700 %	89.50710 %	0.45388 %
	LUMO+2	-2.7944	4.10547 %	0.89219 %	2.81999 %	92.18235 %
	LUMO+3	-2.6008	1.22397 %	1.12417 %	0.32750 %	97.32437 %
	LUMO+4	-2.5609	7.18774 %	19.50195 %	60.74960 %	12.56071 %

			Тра	Phen
	HOMO-3	-6.4327	43.67697 %	56.32303 %
	HOMO-2	-6.4296	95.21991 %	4.78009 %
	HOMO-1	-5.2895	90.27070 %	9.72930 %
	НОМО	-5.1783	31.72876 %	68.27124 %
Phen-Tpa	LUMO	-1.4515	12.00736 %	87.99264 %
	LUMO+1	-1.2138	81.69803 %	18.30197 %
	LUMO+2	-0.4883	90.28856 %	9.71144 %
	LUMO+3	-0.3302	94.28755 %	5.71245 %
	LUMO+4	-0.3175	98.66307 %	1.33693 %

Table S4. Calculated energy levels, and orbital transition analyses for Phen-Tpa and complex **1** in the optimized S_1 and T_1 geometries at the PBE0/6-31G*/LANL2DZ Levels.

complexes	states	Energy	$\lambda_{cal} (nm)$	Main contributions	ILCT	ILLE
		(eV)				
	S ₁	2.7876	444.83	H→L(96.24%)	54.46%	45.54%
	T ₁	1.8519	669.58	H→L(68.66%)	19.41%	80.59%
				H-2→L(9.98%)		
Phen-Tpa	T ₂	2.4959	496.81	H-1→L(48.39%)	45.87%	54.13%
				H→L+2(18.94%)		
	T ₃	2.9160	425.24	H-3→L+1(38.05%)	19.93%	80.07%
				H-2→L(14.54%)		
				H→L(8.50%)		
	S ₁	1.7806	696.39	H→L(98.56%)	81.43%	18.57%
	T ₁	1.7016	728.73	H→L(77.98%)	53.61%	43.32%
1				H-3→L(8.83%)		
	T ₂	2.0255	612.19	H-1→L(81.03%)	67.35%	6.81%
				H→L+4(3.61%)		

Table S5. Compositions of hole and electron for the S_1 states of Phen-Tpa, complex **1** in the optimized S_1 structure.

		Ag	Тра	Phen	Xantphos
	Hole	0.00265 %	99.21959 %	0.77331 %	0.00445 %
1	electron	1.42817 %	17.79240 %	78.74921 %	2.03022 %
	difference	-1.42552%	81.42719%	-77.9759%	2.02577%
	Hole		89.13631 %	10.86369 %	
Phen-Tpa	electron		34.67680 %	65.32320 %	
	difference		54.45951%	-54.45951%	

Table S6. Compositions of hole and electron for the T_1 states of Phen-Tpa, complex **1** in the optimized T_1 structure.

	Ag	Тра	Phen	Xantphos
Hole	0.05277 %	79.15509 %	20.54891 %	0.24323 %

1	electron	1.27579 %	22.77347 %	74.16161 %	1.78913 %
	difference	-1.22302%	56.38162%	-53.61270%	-1.54590%
	Hole		63.38140 %	36.61860 %	
Phen-Tpa	electron		43.96646 %	56.03354 %	
	difference		19.41494%	-19.41494%	

7. Photophysical Measurements

Figure S7 Transient PL decay spectra of Phen-Tpa and 1 in MeOBP films (0.05 Wt%) at 298K.

Figure S8 (a) PL spectra of Phen-Tpa and 1, (b) Transient PL decay spectra of Phen-Tpa and 1, (c)

Time-resolved PL spectra of Phen-Tpa (d) Time-resolved PL spectra of **1** at 77 K doped into MeOBP films (0.05 wt%).

Figure S9 (a) PL spectra, (b) Transient PL decay spectra of Phen-Tpa and **1** in CH₂Cl₂ dilute solution at 298 K.

Table S7. Photophysical parameters of Phen-Tpa and complex 1 in CH₂Cl₂ dilute solution at 298 K.

Compound	λ_{max} (nm)	Φ _{PL} (%)	$\tau_{\rm F}$ (ns)	k _F (s ⁻¹)
Phen-Tpa	490	100	2.68	3.7×10 ⁸
1	546	100	3.62	2.8×10 ⁸

The rate of ISC, RISC can be calculated from the experimental data as follow¹²: 1

$\kappa_p = \frac{\tau_p}{\tau_p}$	(1)
$k_d = \frac{1}{\tau_d}$	(2)
$k_{ISC} = \left(1 - \frac{\Phi_F}{\Phi}\right) k_P$	(3)

$$k_{RISC} = \frac{k_P k_d \Phi_{TADF}}{k_{ISC} \Phi_F} \tag{4}$$

Where τ_P is the transient decay time of the prompt component, τ_d is the transient decay time of the delayed component, Φ_F and Φ_{TADF} are the prompt and delayed components of the PL quantum efficiency, respectively.

To calculate k_{ISC} and k_{RISC} for complex **1**, we first need to determine Φ_F and Φ_{TADF} . In the transient PL decay spectra of complex **1**, the delayed fluorescence completely decays within 100 ms. Therefore, the emission beyond 100 ms can be considered phosphorescence, while the emission before 100 ms consists of both fluorescence and delayed fluorescence. Their respective proportions are estimated to be 0.41 and 0.59 based on the integrated area ratio (Figure S10a). Furthermore, from the transient PL decay spectra of delayed fluorescence in complex **1**, the proportions of delayed fluorescence and fluorescence are estimated to be 0.48 and 0.11, respectively (Figure

S10b). Using Φ_{PL} along with these fluorescence and delayed fluorescence ratios, Φ_{TADF} and Φ_{F} are calculated to be 0.409 and 0.093, respectively. Using Equations 3 and 4, k_{ISC} and k_{RISC} are determined to be 4.0 × 10⁸ s⁻¹ and 358.7 s⁻¹, respectively.

Figure S10 (a) Transient PL decay spectra of complex **1** and the proportions of (i) the total delayed fluorescence and fluorescence and (ii) phosphorescence, calculated based on the integrated area; (b) Transient PL decay spectra of delayed fluorescence in complex **1** and the proportions of delayed fluorescence, fluorescence calculated based on the integrated area.

The temperature-dependent transient PL decay curves of complex **1** were measured as shown in Figure S10, the results indicate that the delayed fluorescence of compound **1** disappears at 158 K, while the phosphorescence exists from 298 K to 77 K. In this case, we can apply a Boltzmann-type equation to characterize the temperature dependence of the emission decay time $\tau(T)$ according to^{13,14}

$$\tau(T) = \frac{3 + exp\left(-\frac{\Delta E(S_1 - T_1)}{k_B T}\right)}{3k(T_1) + k(S_1)exp\left(-\frac{\Delta E(S_1 - T_1)}{k_B T}\right)}$$

Herein, $\Delta E(S_1-T_1)$ refers to the energy separation between the S_1 and T_1 states. $k(S_1)$ and $k(T_1)$ are the rates of the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transition, respectively. k_B is the Boltzmann constant. We selected the delayed fluorescence lifetime of complex **1** from 298 K to 178 K and the phosphorescence lifetime from 158 K to 77 K as fitting data. The fitting results are shown in the figure below. The fitted ΔE_{ST} value (0.195 eV) agrees well with both the calculated value by TD-DFT (0.08 eV) and the estimated value from the emission spectra (0.2 eV).

Figure S11 (a) Temperature dependence of delayed fluorescence decay times for complex **1** (178–278 K); (b) Temperature dependence of phosphorescence decay times for complex **1** (98–278 K); (c) emission decay time vs temperature (red dots) and the fit (red line) of complex **1**.

8. NMR、 Mass and HPLC spectra

Figure S12 ¹H NMR spectrum of complex Phen-Tpa in DMSO-d6.

Figure S13 ¹³C NMR spectrum of complex Phen-Tpa in DMSO-d6.

Figure S14 ¹H NMR spectrum of complex 1 in DMSO-d6.

Figure S15 ¹³C NMR spectrum of complex 1 in DMSO-d6.

Figure S16 Mass spectra of complex 1.

Figure S17 The HPLC spectra of the THF-dissolved **Phen-Tpa** monitored at 290 nm with the acetonitrile-water-THF mixed eluent. Generally, 2 mg of **Phen-Tpa** was dissolved in 30 ml of THF, 5 uL of the solution was then added into the 1 mL of eluent with certain ratio.

9. Reference

(1) M. Louis, H. Thomas, M. Gmelch, A. Haft, F. Fries and S. Reineke, Blue-Light-Absorbing Thin Films Showing Ultralong Room-Temperature Phosphorescence, Adv. Mater. 2019, 1807887.

(2) Sheldrick, G. M. SHELXS-2014/7 and SHELXL-2014/7 Program for Solution and Refinement of Crystal Structures; Institute forInorganic Chemistry, University of Göttingen: Göttingen, Germany, 2014.

[3] M. Thelakkat, H.-W. Schmidt. Synthesis and Properties of Novel Derivatives of 1,3,5Tris(diarylamino)benzenes for Electroluminescent Devices. Adv. Mater. 1998, 10, 219-223.

[4] A. Jouaiti, L. Ballerini, H. L. Shen, R. Viel, F. Polo, N. Kyritsakas, S. Haacke, Y. T. Huang, C. W. Lu,
C. Gourlaouen, H. C. Su, M. Mauro. Binuclear Copper(I) Complexes for Near-Infrared Light-Emitting Electrochemical Cells. Angew. Chem. Int. Ed. 2023, 62, e202305569.

[5] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;
Scalmani, G.;Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.
P.; Izmaylov, A. F.;Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.;
Hasegawa, J.; Ishida, M.;Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J.
A.; Peralta, J. E.; Ogliaro, F.;Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.;
Keith, T.; Kobayashi, R.; Normand, J.;Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.;
Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo,
C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.;
Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg,
J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski J.; and Fox, D. J.;
Gaussian 09, Revision D.01; Gaussian, Inc., Wallingford, CT, 2009.

[6] Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U., Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange. Chem. Phys. 2009, 356 (1), 98-109.

[7] Izsák, R.; Neese, F., An overlap fitted chain of spheres exchange method. J. Chem. Phys. 2011, 135 (14), 144105.

[8] Izsák, R.; Neese, F.; Klopper, W., Robust fitting techniques in the chain of spheres approximation to

the Fock exchange: The role of the complementary space. J. Chem. Phys. 2013, 139 (9), 094111.

[9] Helmich-Paris, B.; de Souza, B.; Neese, F.; Izsák, R., An improved chain of spheres for exchange algorithm. J. Chem. Phys. 2021, 155 (10), 104109.

[10] F. Neese., Software update: The ORCA program system—Version 5.0. WIREs Comput Mol Sci. 2022; 12:e1606.

[11] Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580-592.

[12] K. Wang, W. Liu, C.-J. Zheng, Y.-Z. Shi, K. Liang, M. Zhang, X.-M. Ou and X.-H. Zhang, A comparative study of carbazole-based thermally activated delayed fluorescence emitters with different steric hindrance, J. Mater. Chem. C, 2017, 5, 4797-4803.

[13] Highly Efficient OLEDs: Materials Based on Thermally Activated Delayed Fluorescence; Yersin, H., Ed.; WILEY-VCH: Weinheim, Germany, 2019.

[14] M. Klein, N. Rau, M. Wende, J. Sundermeyer, G. Cheng, C.-M. Che, A. Schinabeck and H. Yersin, Cu(I) and Ag(I) Complexes with a New Type of Rigid Tridentate N, P, P-Ligand for Thermally Activated Delayed Fluorescence and OLEDs with High External Quantum Efficiency, Chem. Mater, 2020, **32**, 10365.