Modulation of the luminescence quantum efficiency for blue luminophor {Al(salophen)}$^+$ by ester-substituents

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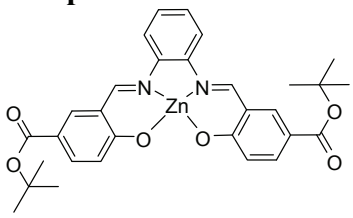
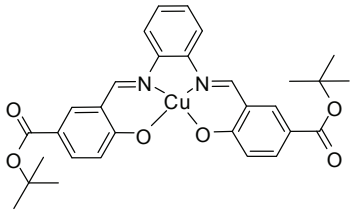
Content:

Synthetic details for Zn and Cu complexes 5b and 6b



N,N'-bis-(3-tert-butoxycarbonylsalicylidene)-1,2-phenylenediamine zinc (II).H_2O (5b): A suspension of **3b** (93 mg; 0.18 mmol) in 18 mL of methanol was prepared. To this suspension, a solution of $Zn(OAc)_2.2H_2O$ (39.3 mg; 0.18 mmol) in 12 mL of methanol was added dropwise. The resulting mixture was then refluxed for 2h and cooled down to room temperature. The yellow precipitate obtained was isolated by filtration, washed with water and dried under vacuum (84 mg, 82%). Anal. Calcd for $C_{30}H_{30}N_2O_6Zn.H_2O$: C, 60.26; H, 5.39; N, 4.68. Found: C, 60.60, H, 5.22, N, 5.11. ^{1}H NMR ($(CD_3)_2CO$) δ 9.15 (2H, s, HC=N), 8.16 (2H, d, Ar-H), 8.00 (2H, m, Ar-H), 7.76 (2H, dd, Ar-H), 7.48 (2H, m, Ar-H), 6.74 (2H, d, Ar-H), 1.57 (18H, s, CH_3). ν_{max}/cm^{-1} 1710 (COO), 1613 (C=N).



N,N'-bis-(3-tert-butoxycarbonylsalicylidene)-1,2-phenylenediamine copper (II).CH_3OH (6b)*:* To a suspension of **3b** (93 mg; 0.18 mmol) in 18 mL of methanol, a solution of $Cu(OAc)_2.H_2O$ (35.4 mg; 0.18 mmol) in 12 mL of methanol was added dropwise. The resulting mixture was then refluxed for 2h and cooled down to room temperature. The brown precipitate obtained was isolated by filtration, washed with water and dried under vacuum (63 mg, 61%). Anal. Calcd for $C_{30}H_{30}N_2O_6Cu.3CH_3OH$: C, 58.79; H, 6.28; N, 4.15. Found: C, 58.48, H, 6.21, N, 4.39. ν_{max}/cm^{-1} 1712 (COO), 1611 (C=N).

Table 1-ESI. Experimental and crystal data for **PyO-4b**

Formula	$C_{40}\ H_{46}\ Al\ N_5\ O_{14}$
Formula weight	847.80
Asymmetric unit cont.	$C_{40}\ H_{46}\ Al\ N_5\ O_{14}$
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.256(3) Å
	b = 12.790(3) Å
	c = 14.959(4) Å
	α= 68.740(10)°
	β= 70.910(10)°.
	γ = 81.620(10)°.
Volume	2064.1(9) $Å^3$
Density (calculated)	1.364 Mg/m^3
Absorption coefficient	0.123 mm^{-1}
Theta range for data collection	3.41 to 22.72°.
Index ranges	-13≤ h ≤12
	-13≤ k ≤13
	-16≤ l ≤=16
Reflections collected	8854
Independent reflections	5294 [R(int) = 0.0809]
Completeness to theta = 22.72°	95.3 %
Data / restraints / parameters	5294 / 0 / 547
Goodness-of-fit on F^2	0.970
Final R indices [I>2sigma(I)]	R1 = 0.0735
	wR2 = 0.1714
R indices (all data)	R1 = 0.1531
	wR2 = 0.2186
Largest diff. peak and hole	0.544 and -0.363 $e.Å^{-3}$

Table 2-ESI. Photophysical data of Schiff bases **3a-c** (λ_{exc} = 385 nm, 5.0×10^{-6}M in DMSO)

	Absorption		Emission	
Schiff base	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (nm)	$\phi^{[a]}$ (%)
(R = CH_3)				
3a	310	26000	474	3
	382	12000		
	420	8600		
(R = $(CH_3)_3C$)				
3b	334	19280	481	1
	382	20400		
(R = C_6H_5)				
3c	278	36800	478	7
	332	8000		
	378	7600		

[a] Quinine sulfate (ϕ = 0.55) used as standard

Table 3-ESI. Photophysical data of complexes **5b** (Zn) and **6b** (Cu) (λ_{exc} = 385 nm, 5.0×10^{-6}M in DMSO)

	Absorption		Emission	
Complexes	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (nm)	$\phi^{[a]}$ (%)
5b	290	73200	478	0.2
	390	21100		
6b	293	103000	478	0.04
	411	19800		

[a] Quinine sulfate (ϕ = 0.55) used as standard

Table 4-ESI. Photophysical data of salophen and its complexes of Al, Zn, and Cu (λ_{exc} = 378 nm , 5.0×10^{-6}M in DMSO).

Compound	λ_{max} (nm)	λ_{em} (nm)	$\phi^{[a]}$
salophen	269, 350	501	0.003
Al(NO_3)salophen	284, 338, 390	490	0.01
Znsalophen	289, 340 (sh), 404	490	0.002
Cusalophen	284, 427	490	0.002

[a] Quinine sulfate (ϕ = 0.55) used as standard

Table 5-ESI Most important electronic transitions (nm) computed for **4b** and **4c**, with the associated oscillator strength (a threshold of 0.01 has been used for the reported oscillator strength).

4b		**4c**	
λ_{calcd}	f_{calcd}	λ_{calcd}	f_{calcd}
413	**0.442**	**416**	**0.494**
382	0.014	382	0.015
368	**0.397**	**369**	**0.417**
352	0.024	352	0.014
336	**0.329**	**336**	**0.251**
322	0.055	331	0.080
312	**0.470**	**322**	**0.058**
302	0.041	312	0.445
266	**0.447**	**308**	**0.017**
263	0.081	301	0.036
256	0.141	279	0.029
251	0.015	**278**	**0.794**
250	**0.852**	277	0.035

Figure 1-ESI. Internal and external quantum yields of *(from top)* **3b**, **4b**, and **5b** calculated from the standard NBS1028 (Zn_2SiO_4 :Mn^{2+}).

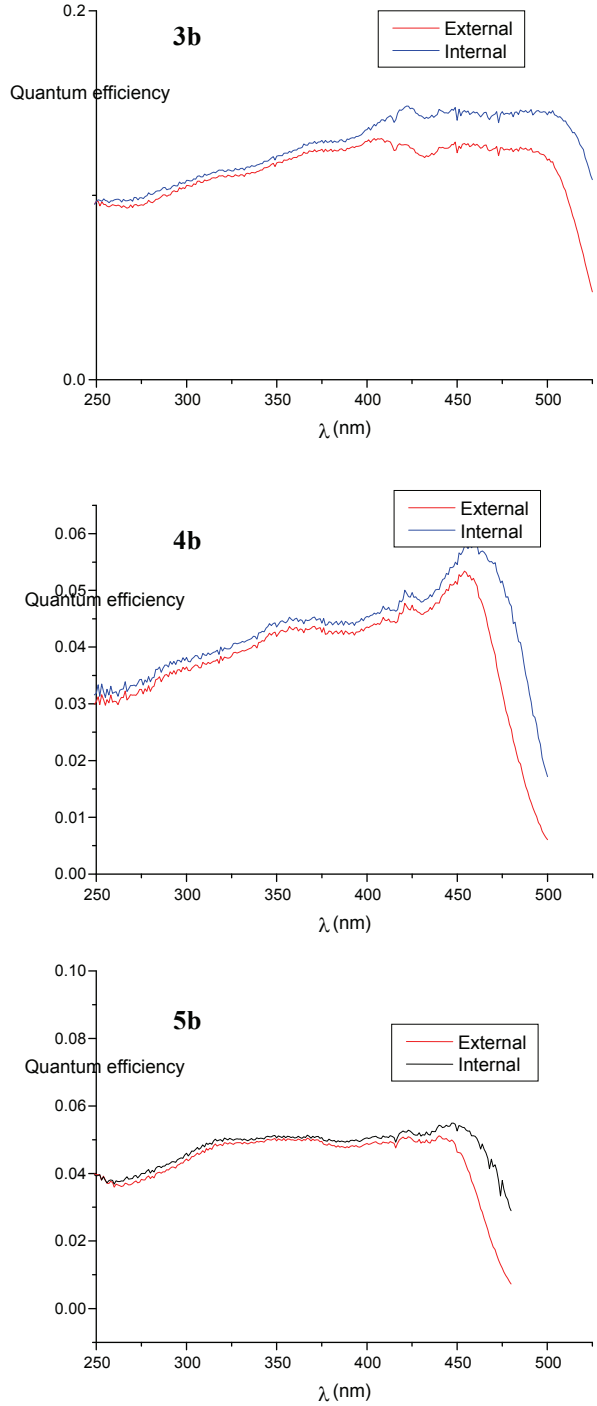


Figure 2-ESI. Trichromatic coordinates diagram (http://www.cie.co.at/index_ie.html)