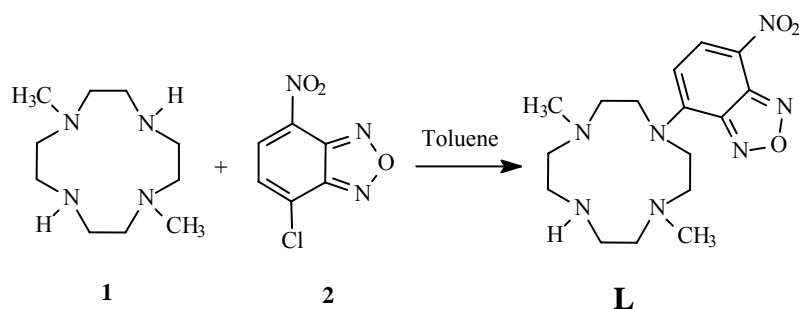


## Synthesis

All chemicals were purchased from Aldrich in the highest quality commercially available. All the solvents were dried prior to use. The 1,7-dimethyl-1,4,7,10-tetraazacyclo-dodecane **1** was prepared as described in ref.: M. Ciampolini, P. Dapporto, M. Micheloni, N. Nardi, P. Paoletti and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1984, 1357.



Scheme of the synthesis

### 4-(4,10-Dimethyl-1,4,7,10-tetraazacyclododec-1-yl)-7-nitrobenzo[1,2,5]oxadiazole (**L**)

A solution (200 cm<sup>3</sup>) of NBD-chloride (**2**) (1 g, 5 mmol) in freshly distilled anhydrous toluene and a solution (200 cm<sup>3</sup>) of 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**1**) (1.0 g, 5 mmol) in freshly distilled toluene were added simultaneously at room temperature to 200 cm<sup>3</sup> of vigorously stirred anhydrous toluene. The addition was completed in eight hours after which the resulting suspension was stirred for a further 2 days. The solid formed was filtered, washed with toluene and dried under vacuum. The orange solid obtained was recrystallized from hot aqueous HCl 3M, obtaining **L**·4HCl (1.5 g, 59%). Anal. Calcd for C<sub>16</sub>H<sub>29</sub>Cl<sub>4</sub>N<sub>7</sub>O<sub>3</sub>: C, 37.74; H, 5.74; N, 19.25. Found: C, 37.7; H, 5.6; N, 19.3. <sup>1</sup>H NMR (D<sub>2</sub>O, pH=2, 25 °C): δ 8.42 (1H, d, *J* = 9.1 Hz), 6.48 (1H, d, *J* = 9.1 Hz), 4.45 (2H, m), 4.15 (2H, m), 3.55 (4H, m), 3.33 (8H, m), 2.93 (6H, s). <sup>13</sup>C NMR (D<sub>2</sub>O, pH=2, 25 °C): δ 146.8, 146.5, 145.5, 137.9, 125.0, 107.4, 57.3, 57.1, 55.9, 51.9, 43.1.

**Table S1.**

Selected bond distances (Å) and bon angles (°) of the complex cation [LCuCl]<sup>+</sup> for **1** and **2**.

	<b>1</b>	<b>2</b>
Bond distances		
Cu(1)-N(1)	2.050(8)	2.061(5)
Cu(1)-N(2)	2.044(9)	2.019(5)
Cu(1)-N(3)	2.037(8)	2.045(6)
Cu(1)-N(4)	2.118(8)	2.142(5)
Cu(1)-Cl(1)	2.427(3)	2.376(2)
Bond angles		
Cl(1)-Cu(1)-N(1)	105.2(3)	106.8(2)
Cl(1)-Cu(1)-N(2)	97.1(3)	98.0(2)
Cl(1)-Cu(1)-N(3)	105.6(2)	103.0(2)
Cl(1)-Cu(1)-N(4)	117.7(3)	116.1(2)
Cu(1)-N(1)-C(9)	116.3(7)	113.9(4)
Cu(1)-N(3)-C(10)	112.9(7)	115.9(5)
Cu(1)-N(4)-C(11)	120.2(7)	122.2(4)

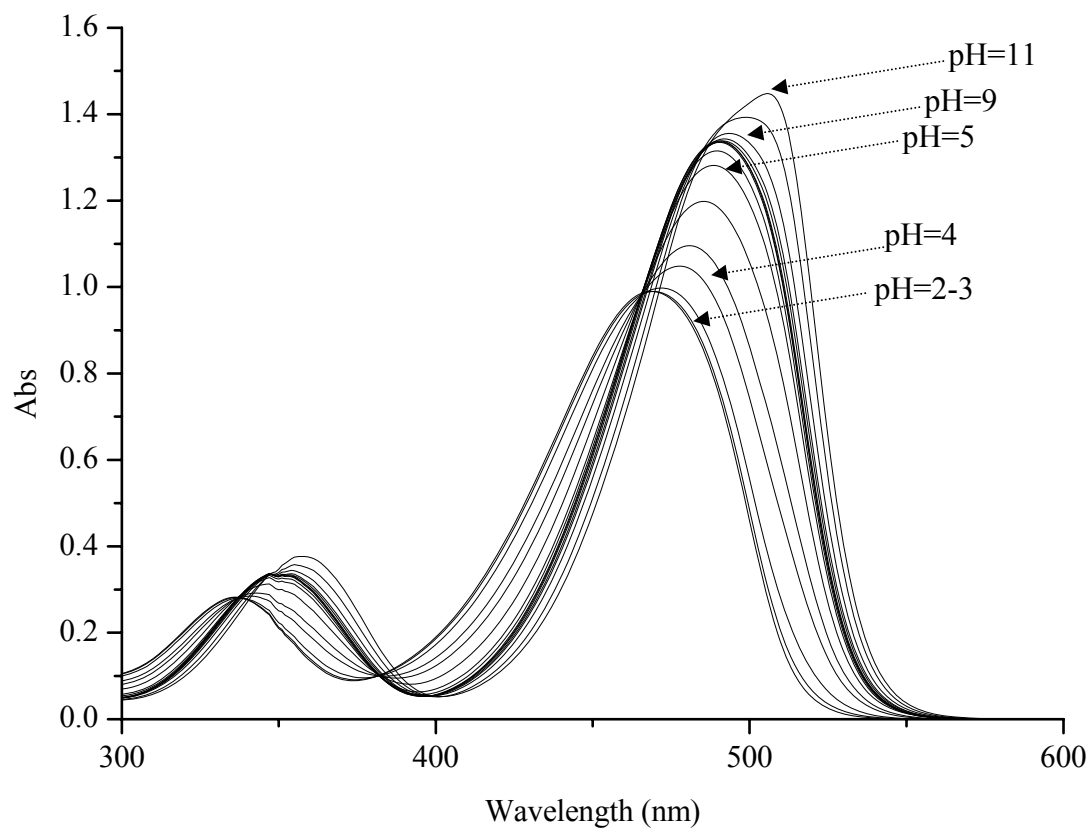
**Table S2.**

Intermolecular contacts in **1** and **2**.

	NH $\cdots$ O distance (Å)	NHO angle (°)
<b>1</b>		
N(2)-H(2n) $\cdots$ O(11)	2.35(1)	147.5(6)
<b>2</b>		
N(2)-H(2n) $\cdots$ O(1w)	2.83(1)	125.3(4)
N(2)-H(2n) $\cdots$ N(6) <sup>'</sup>	2.420(6)	129.5(4)

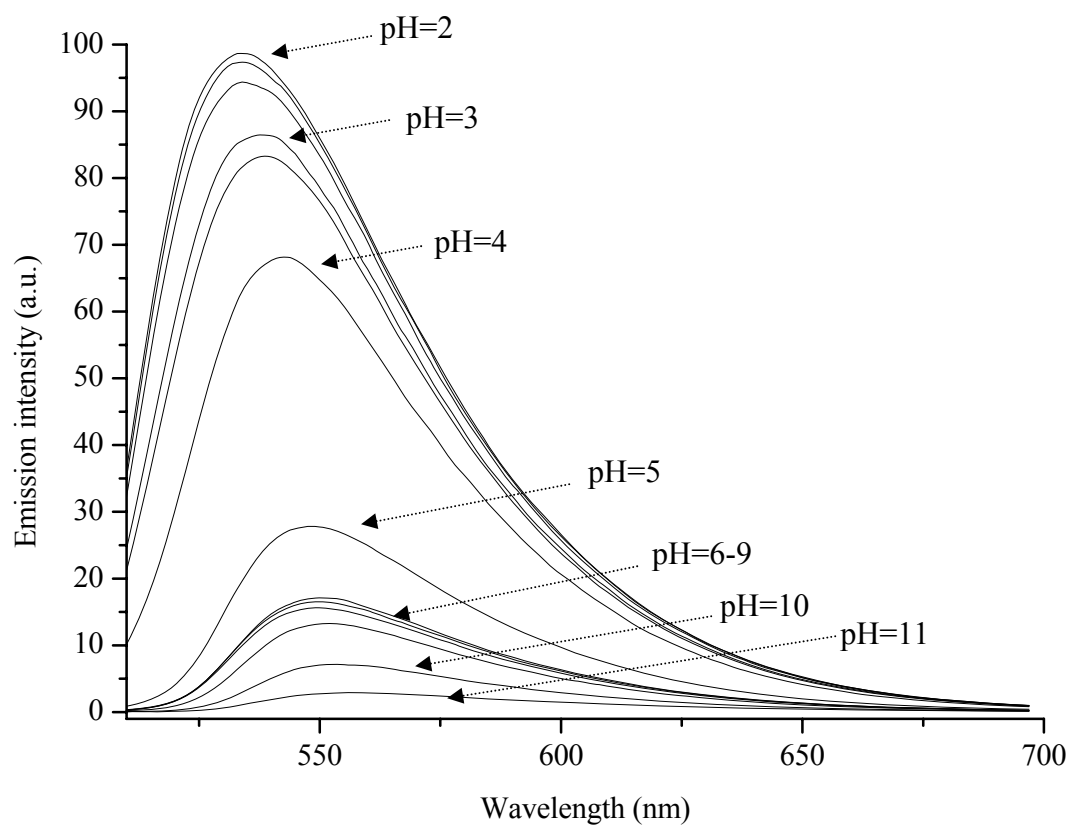
<sup>'</sup> = x+1, -y+0.5, z+0.5

**Figure S1**



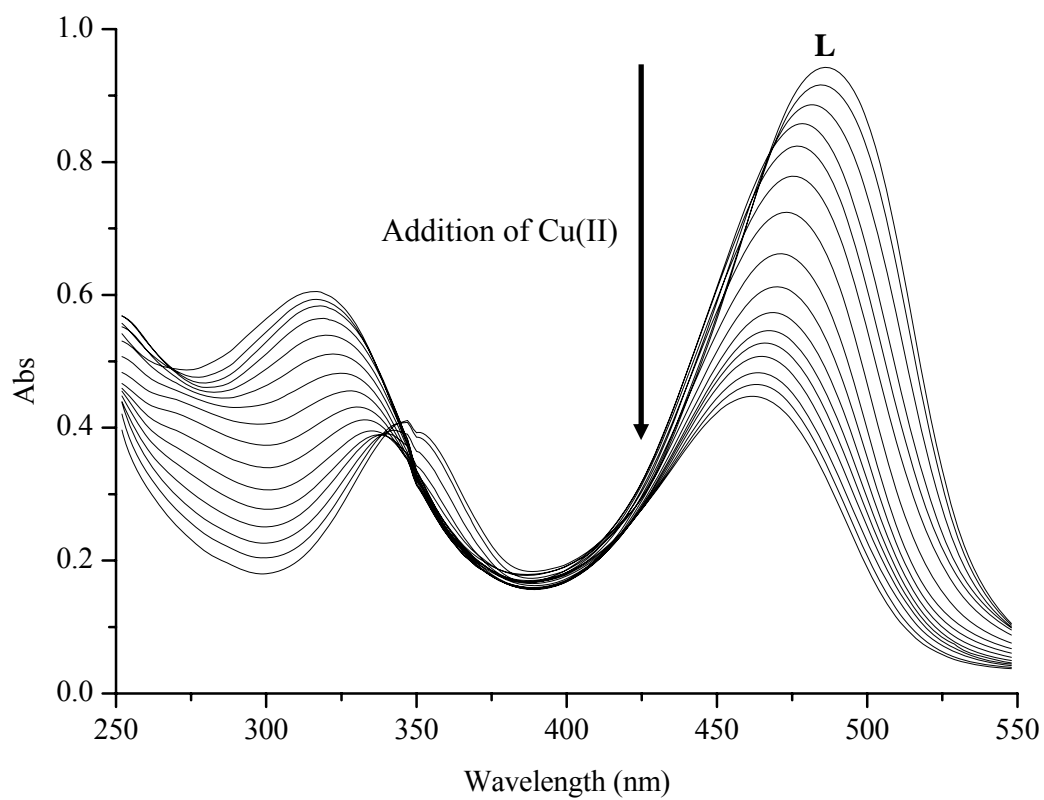
Variation of the absorption spectra of **L** in 0.15 M NMe<sub>4</sub>Cl aqueous solution at various pH values.  
[**L**]=5x10<sup>-5</sup> M.

**Figure S2**



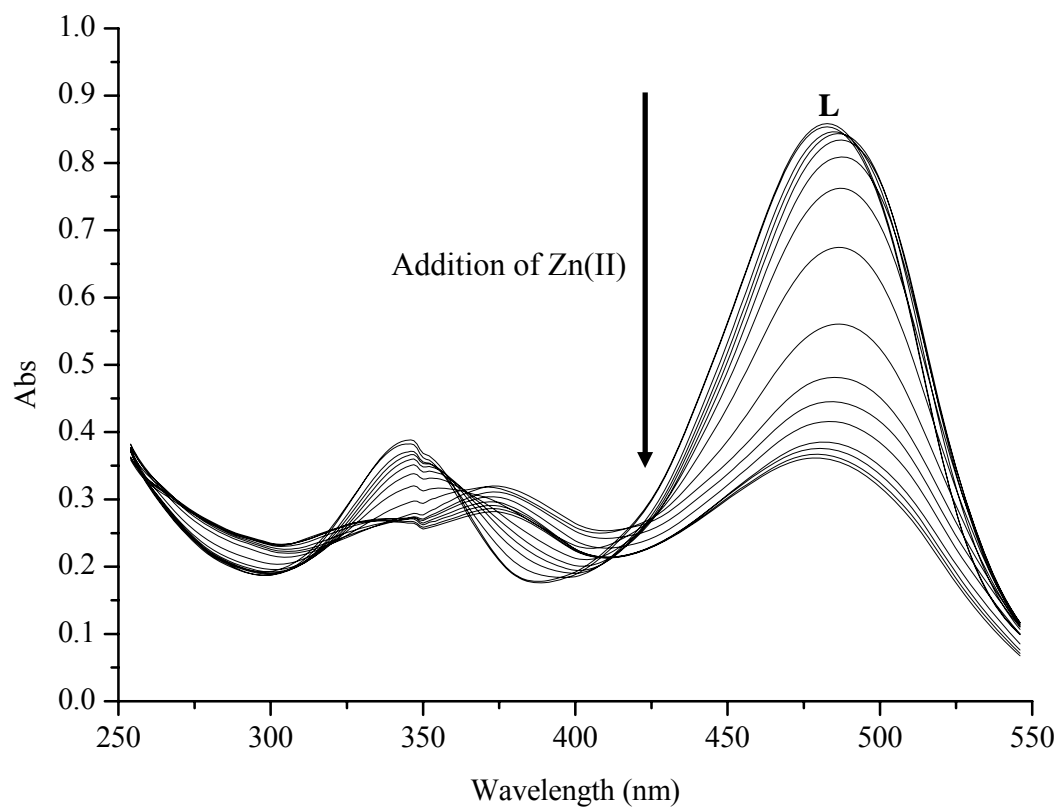
Variation of the emission spectra of **L** in 0.15 M NMe<sub>4</sub>Cl aqueous solution at various pH values.  
[**L**]=5×10<sup>-6</sup> M, λ<sub>ex</sub>=476 nm.

**Figure S3**



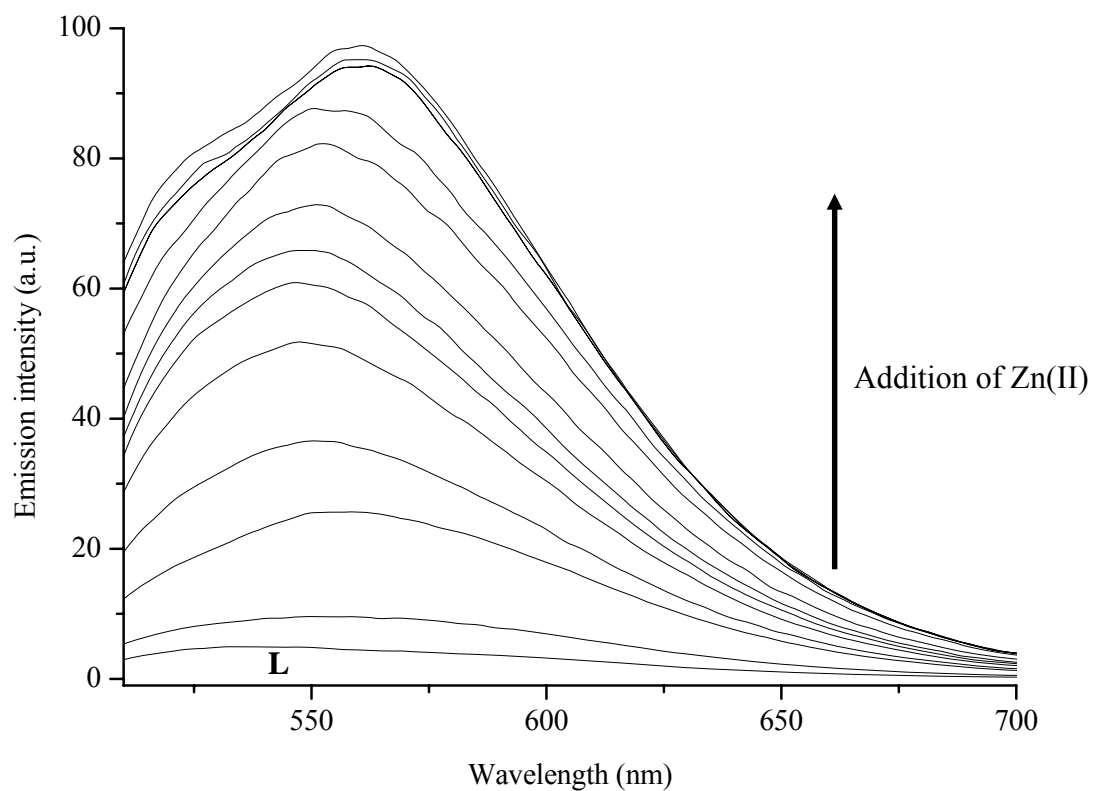
Variation of the absorption spectra of **L** in acetonitrile by adding  $\text{Cu(ClO}_4)_2$ :  $[\text{L}] = 5 \times 10^{-5} \text{ M}$ ,  $[\text{Cu}^{2+}] =$  from 0 to  $5 \times 10^{-5} \text{ M}$ .

**Figure S4**



Variation of the absorption spectra of **L** in acetonitrile by adding  $\text{Zn}(\text{ClO}_4)_2$ :  $[\text{L}] = 4.5 \times 10^{-5} \text{ M}$ ,  $[\text{Zn}^{2+}] =$  from 0 to  $4.5 \times 10^{-5} \text{ M}$ .

**Figure S5**



Variation of the emission spectra of **L** in acetonitrile by adding  $\text{Zn}(\text{ClO}_4)_2$ :  $[\text{L}] = 10^{-5} \text{ M}$ ,  $[\text{Zn}^{2+}] =$  from 0 to  $10^{-5} \text{ M}$ ,  $\lambda_{\text{ex}} = 486 \text{ nm}$ .