Tetrasubstituted copper phthalocyanines : correlation between liquid crystalline properties, films alignment and sensing propertie

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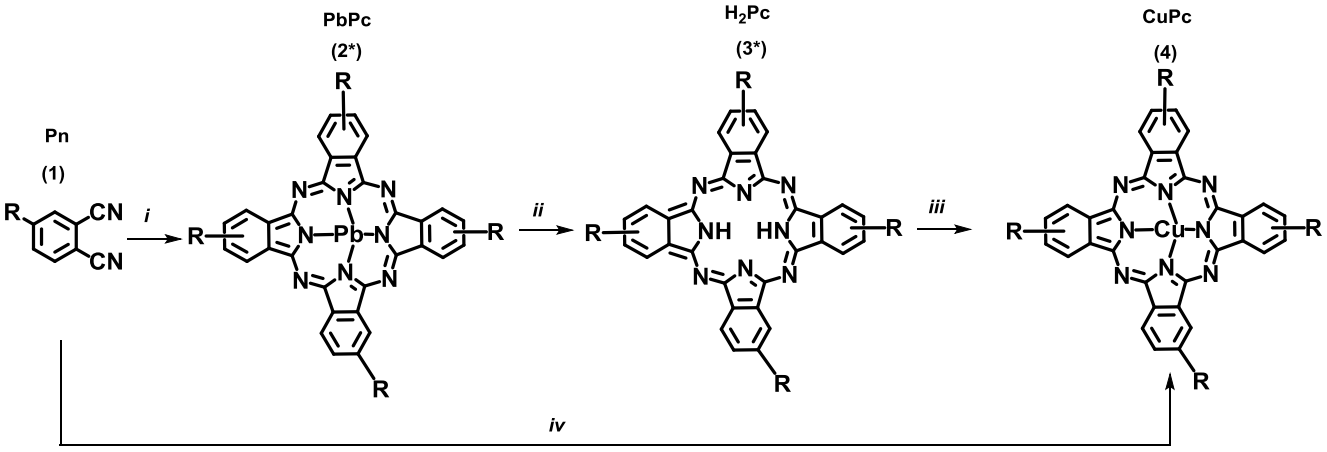

R	Pn (1)	PbPc (2*)	H_2Pc (3*)	CuPc (4)	Synthetic Route
$-OC_8H_{17}$	1a	2a	3a	4a	*i, ii, iii*
$-O_{16}H_{33}$	1b	2b	3b	4b	*i, ii, iii*
$-SC_8H_{17}$	1c	2c	3c	4c	*i, ii, iii*
$-SC_{16}H_{33}$	1d	2d	3d	4d	*i, ii, iii*
$-O(CH_2CH_2O)_3CH_3$	1e			4e	*iv*
$-S(CH_2CH_2O)_3CH_3$	1f			4f	*iv*

Figure 1. Synthesis of CuPc derivatives, **4a-4c**, **4d** [34], **4e-f** [35]. *i*: anhydrous PbO, solvent-free, 210°C, 5h. *ii*: CH_3COOH. *iii*: anhydrous $CuCl_2$, anhydrous n-hexanol, reflux, 2h. *iv*: anhydrous $CuCl_2$, anhydrous n-hexanol, DBU, reflux, 24h. *PbPc (**2**) and H_2Pc (**3**) derivatives were not purified but directly used for the synthesis of CuPc derivatives (**4a-d**).

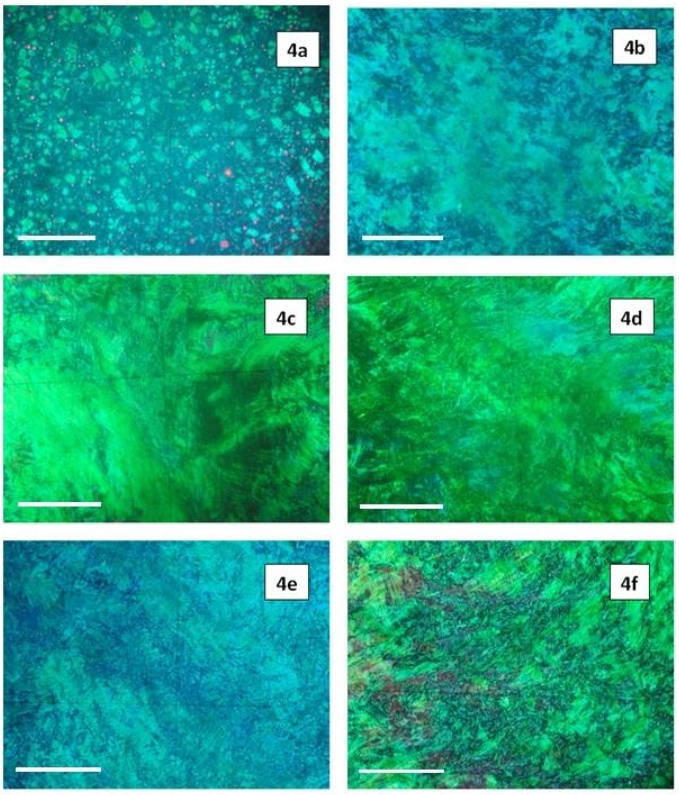

Figure 2. POM images of CuPcs (**4a-f**). The scale bar indicates 100 μm.

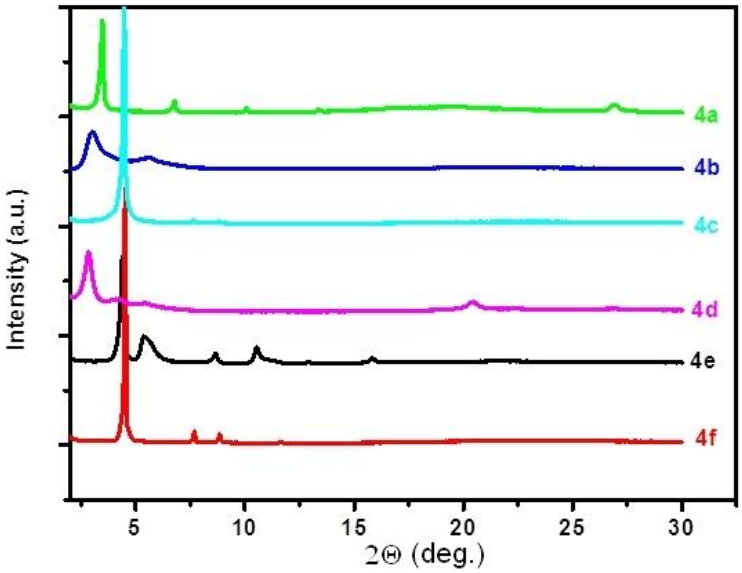

Figure 3. XRD patterns of CuPc derivatives **(4a-f)** measured at room temperature.

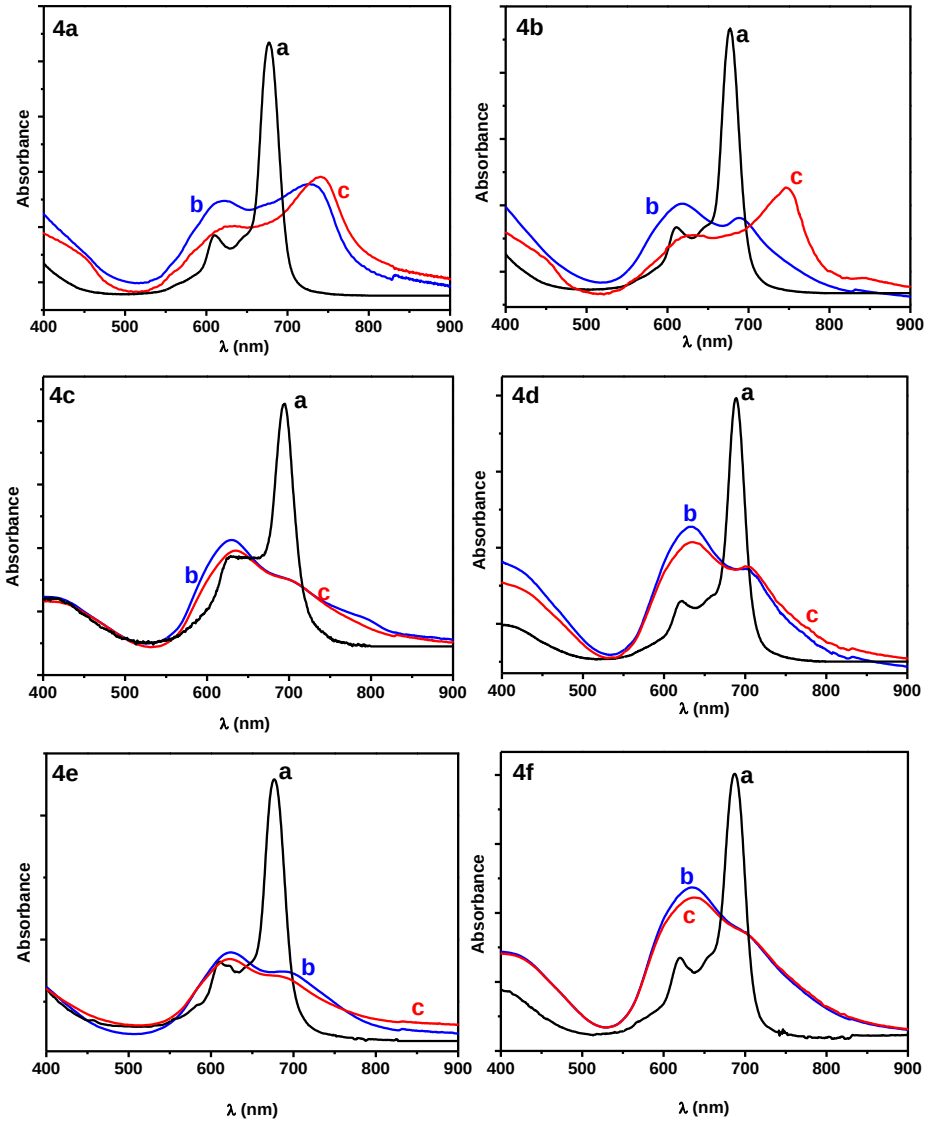

Figure 4. Optical absorption spectra of CuPc **(4a-f)**: solutions in dichloromethane (a), as-deposited films (b), films after heat treatment (c).

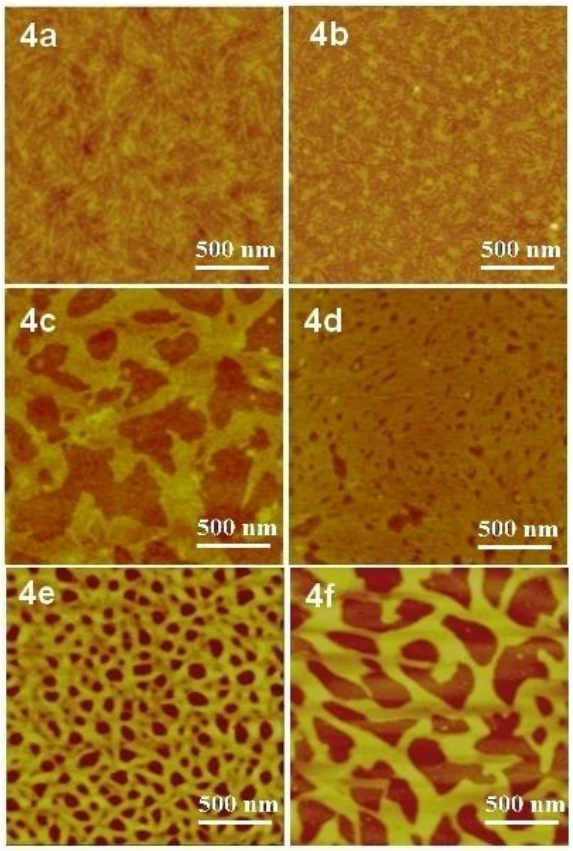

Figure 5. AFM images of the films of CuPcs **(4a-f).**

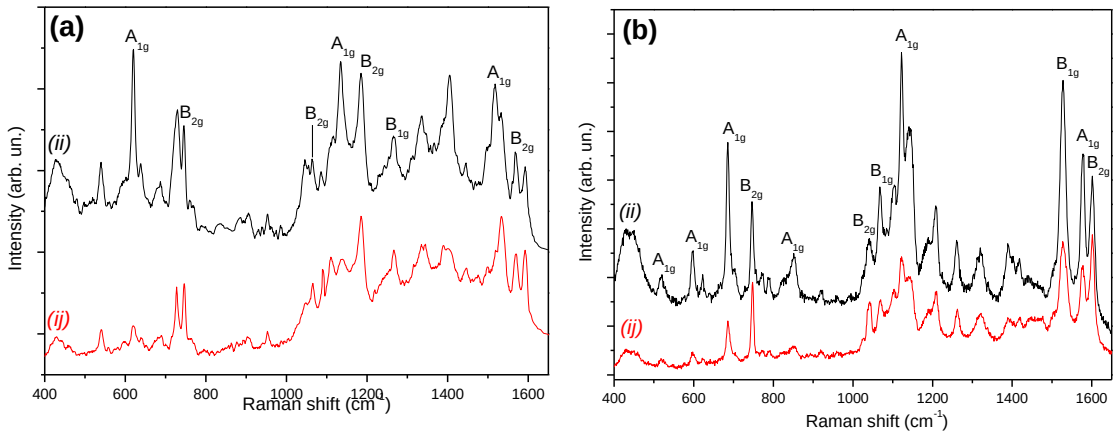

Figure 6. Polarized Raman spectra of **4b** (a) and **4d** (b) films on glass substrates after heat treatment.

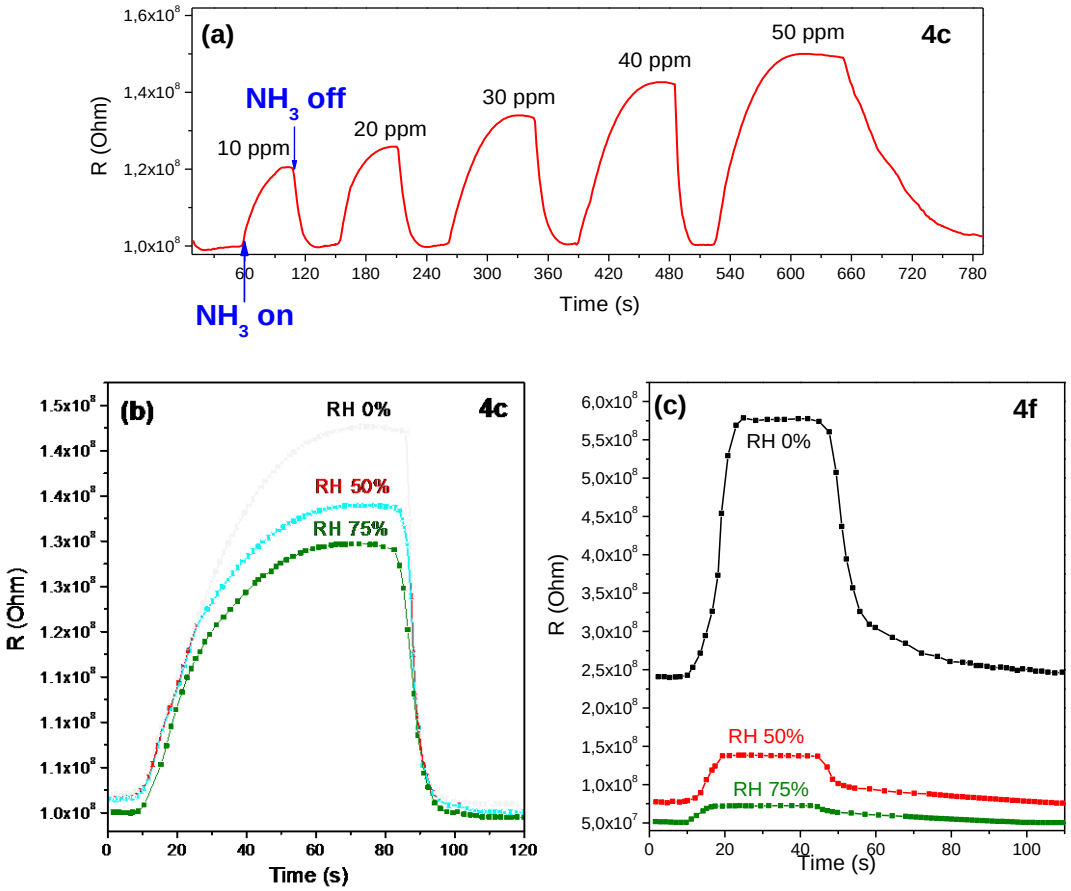

Figure 7. Response curves of the film of **4c** to ammonia vapours at concentrations of 10-50 ppm (a) measured at 50%. Response curves of the films of **4c** (b) and **4f** (c) to ammonia vapours (30 ppm) measured at different relative humidities.

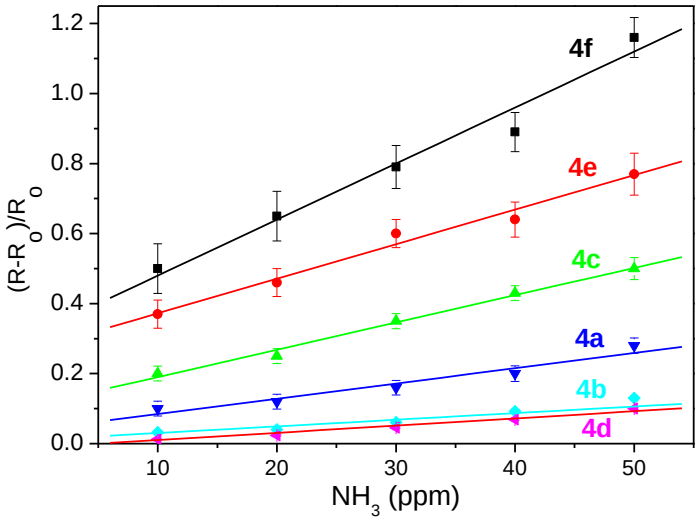

Figure 8. Normalized sensor response vs NH_3 concentration, measured at RH 50%.

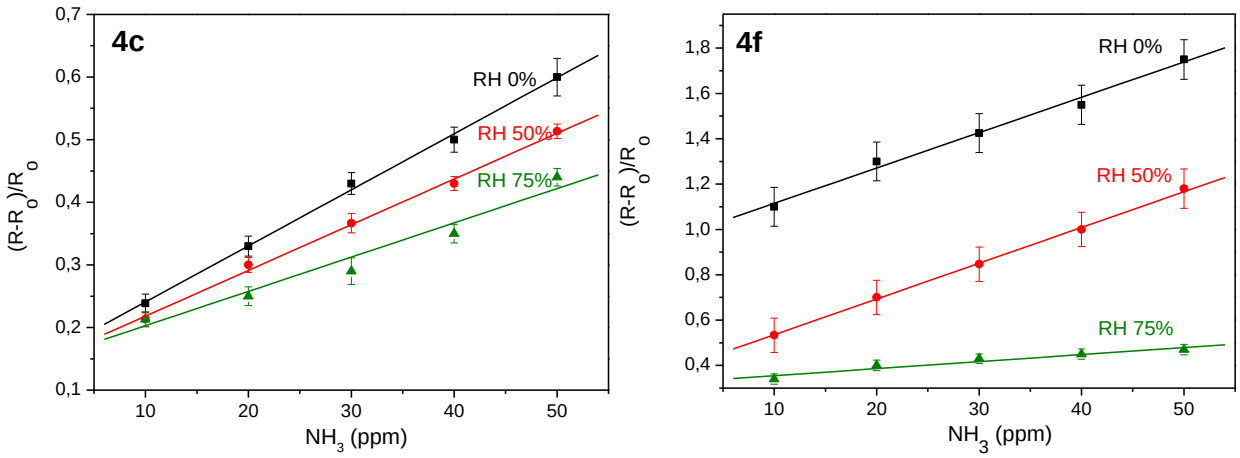

Figure 9. Normalized sensor response of **4c** and **4f** films vs NH_3 concentration, measured at RH 0, 50 and 75%.