

Supplementary information

Enhanced Cl₂ sensitivity of cobalt-phthalocyanine film by utilizing a porous nanostructured surface fabricated on glass

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S1: Purity of CoPc film

CoPc molecules are composed of four indole units, and these indole units contain pyrrole rings with nitrogen atoms conjugated by six-membered benzene ring [S1, S2]. The CoPc film was characterized by various techniques such as FTIR, Raman, UV-Vis spectroscopy etc., to investigate the purity of CoPc thin film. The details are given below:

S1 (a) FTIR spectroscopy

FTIR spectra of CoPc-Etched film were recorded along with CoPc powder. Both the spectra, in the range of (600-1650 cm⁻¹), are presented in the Fig. S1. The experiments were performed in diffusive reflectance mode. To check the purity, band assignments are summarized in Table S1 [S1-S3]. All peaks corresponding C–C stretching vibration in pyrrole, C–C out of ring deformation, β(C–H) aryl, C–H bending in plane deformations, N–H in plain bending vibration etc., are present in FTIR spectra of CoPc film, and the peaks are matching with FTIR

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spectrum of CoPc powder. These results indicate the formation of pure CoPc sample in thin film form.

Table 1: Peak assignments for cobalt phthalocyanine (CoPc) [S1-S3].

	Wave number (cm ⁻¹)	Band assignment
	1610	$\nu(\text{C}-\text{C})$ stretching vibrational of pyrole deformation
	1524	$\nu(-\text{N}=\text{C})$
	1470	C–C stretching in isoindole (ν -isoindole)
	1427	C–C stretching in isoindole (ν -isoindole)
	1334	C–C stretching in isoindole (ν -isoindole)
	1290	C–H in plain deformation ($\delta_{\text{C-H}}$)
	1167	$\delta_{\text{C-H}}$ (in plan + isoindole)
	1121	isoindole totally symm.
	1093	$\delta_{\text{C-H}}$ (in plain)
	1055	$\nu(\text{C}-\text{N})$ in plane
	1003	N–H in plain bending vibrational
	875	δ (isoindole + nitrogen mesoatoms)
	756	δ (Pc ring)
	731	$\delta_{\text{C-H}}$ (out-of-plain)
	617	C–C out of plain ring deformation

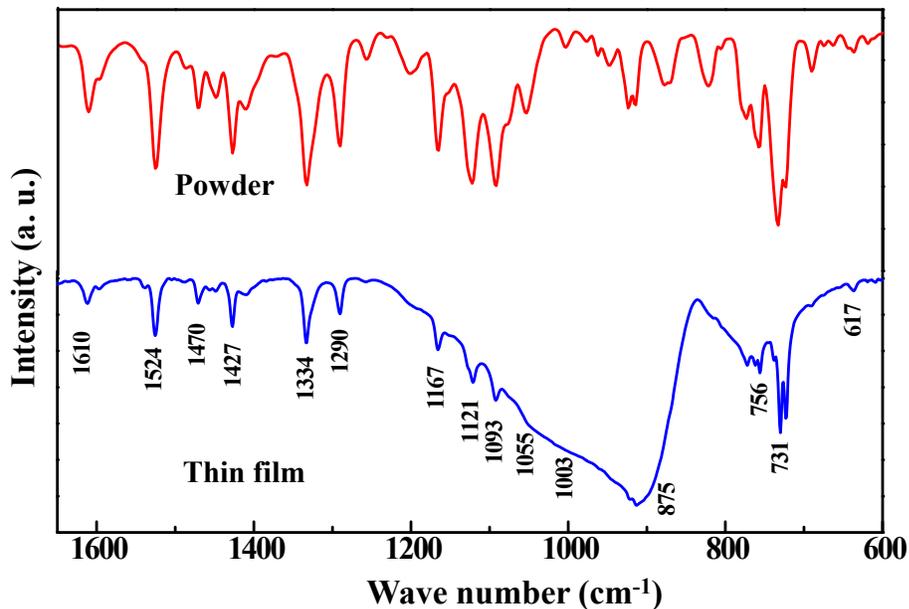


Figure S1: FTIR spectra of CoPc powder and thin film of thickness 60 nm.

S1(b) Raman Spectroscopy

Fig. S2 shows a comparison of Raman spectra of CoPc powder and CoPc film in the wave number region 600-1560 cm^{-1} . The two intense peaks are present in this region at ~ 1541 cm^{-1} and 1340 cm^{-1} for both powder and thin film. The peak present at ~ 1541 cm^{-1} is attributed to the B_1 Raman mode due to large tangential C-N-C bridging bond displacements, while the peak at ~ 1340 cm^{-1} is ascribed to the Co-N symmetric stretching mode in phthalocyanine rings [S4-S5]. The weak peaks at ~ 753 and 965 cm^{-1} are corresponding to the typical C-H out-of-plane vibration and metal (Co)-ligand vibration, respectively. A low intensity peak at ~ 840 cm^{-1} is present in both the spectra, which may be assigned to the stretching of N-Co bond and C-N_{Co}-C bond in plain bending. In both spectra (powder and film), presence of all Raman peaks without any shift indicates the CoPc film deposited on glass substrate in its pure form.

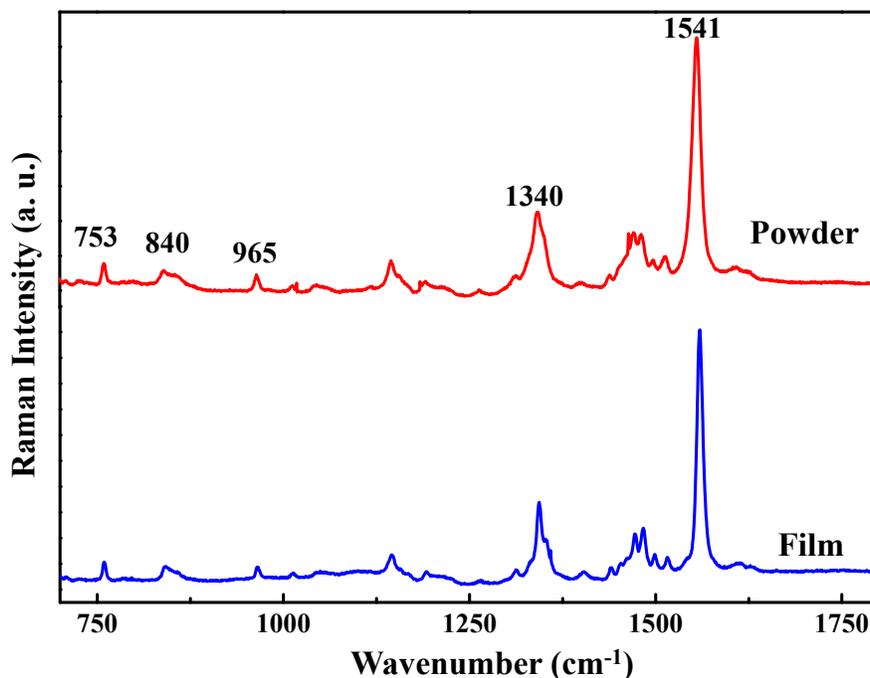


Figure S2: Raman spectra of CoPc powder and thin film of thickness 60 nm.

S1 (c) UV-Vis spectroscopy

The UV-Vis spectra of CoPc film deposited on glass as well as quartz substrate (as glass shows strong absorption in UV region) are presented in Fig. S3. It has been reported that CoPc absorption spectra have two different bands: (i) a single peak UV region (in the range 300-370 nm), which is called Soret band or B-band. (ii) Other is a doublet of close peaks in visible region (550-750 nm), which is called Q-band [S6]. In addition, there is a flat region area in the wavelength range (380-530 nm) is present in spectrum. In Fig. S3, the peaks at 619 and 691 nm can be assigned the doublets of peaks (Q-band), which arises due π - π^* transition between bonding and anti-bonding molecular orbitals. The peak present at 288 nm can be attributed to the B-band. This peak is not observed in CoPc film deposited on etched glass as glass strongly absorbs the UV light. The absorption spectrum of CoPc solution is also presented in Fig S3. It can be seen absorption spectra of CoPc solution shows similar features. These results indicate the purity of deposited film.

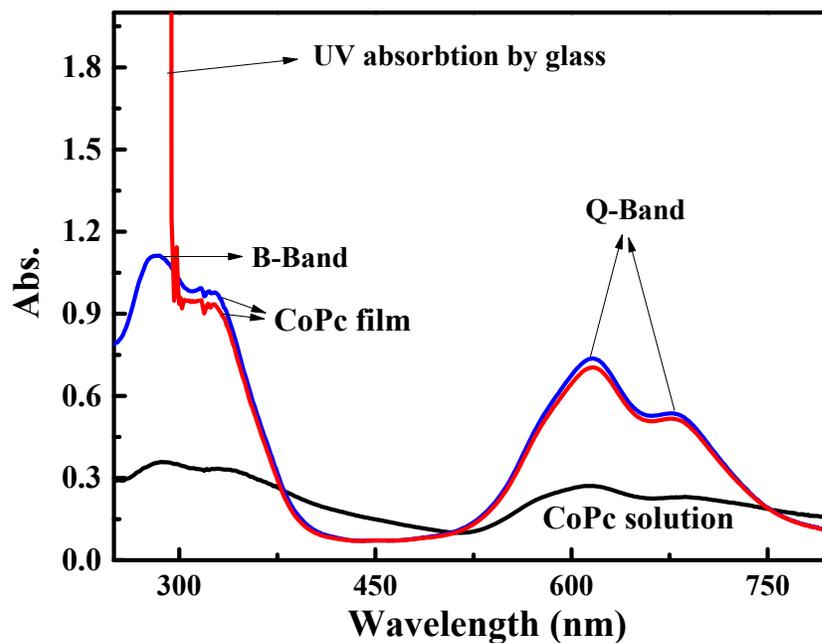


Figure S3: UV-Vis spectra of CoPc film of thickness 60 nm (deposited on glass and quartz) and solution.

S4: X-ray photoelectron spectroscopy

The purity of CoPc film was also characterized by XPS, and the spectra were recorded at three different locations. The obtained spectra have been presented in Fig. S4. In phthalocyanine thin the main peaks are: C 1s, N 1s, O 1s and Co 2p [S7, S8]. A strong peak present at ~285 eV is ascribed to the presence of carbon atom in phthalocyanine ring (C 1s). The peak present at ~400 eV is attributed to the nitrogen (N 1s) of phthalocyanine amine ring. Oxygen can be absorbed by physisorption and/or chemisorption process on the CoPc film surface. The peak (O-1s) at ~532 eV is due to adsorbed oxygen. The peak corresponding to central metal atom (Co-2p) of the phthalocyanine ring appears at ~780 eV. No other impurity peak has been observed.

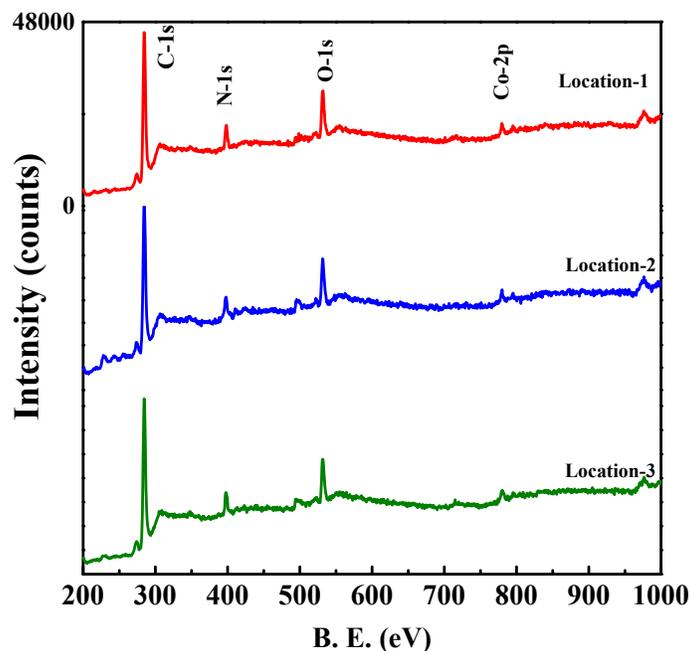


Figure S4: XPS spectra of CoPc film (60 nm) at different locations.

S1 (e) Secondary ion mass spectroscopy (SIMS)

The CoPc film was also investigated by SIMS, which gives the information about the molecular mass. The CoPc film was exposed to high energy Ar ion (5-40 keV). These Ar ions sputter the CoPc film in the form of ionized molecule/their fragments, which are analyzed by time of flight (TOF) mass spectrometer. The SIMS spectrum of CoPc film is shown in the Fig. S5. It can be seen that a strong peak present at ~571 amu, which is corresponding to CoPc molecule (molecular weight 571.3 amu).

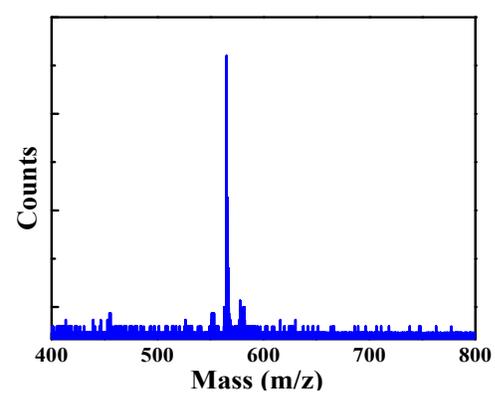


Figure S5: SIMS spectrum of CoPc film.

S2: Elemental distribution in CoPc film

In order to investigate the uniformity distribution the CoPc film was characterized by Raman spectroscopy and XPS. Both XPS and Raman data were recorded at different locations, and the corresponding results are shown in Figs. S4 and S6, respectively. It can be seen that all Raman peak (discussed in S1(b)) of phthalocyanine film are present at all three different location. In addition, the intensity counts per second (cps) of these peaks was found be almost same at every location. In cobalt phthalocyanine central metal atom (Co) is attached to the isoindole group through nitrogen atom. XPS spectra of CoPc film at different locations are shown in Fig. S3. All peaks corresponding to Co, N, and C atoms are present with almost same intensity at all three locations. In addition, for every location, the value of relative intensity ratio $I_{N\ 1s}/I_{Co\ 2p}$ of the N 1s and Co 2p peaks was found to be same. These results suggest that the elemental distribution is almost uniform in CoPc film.

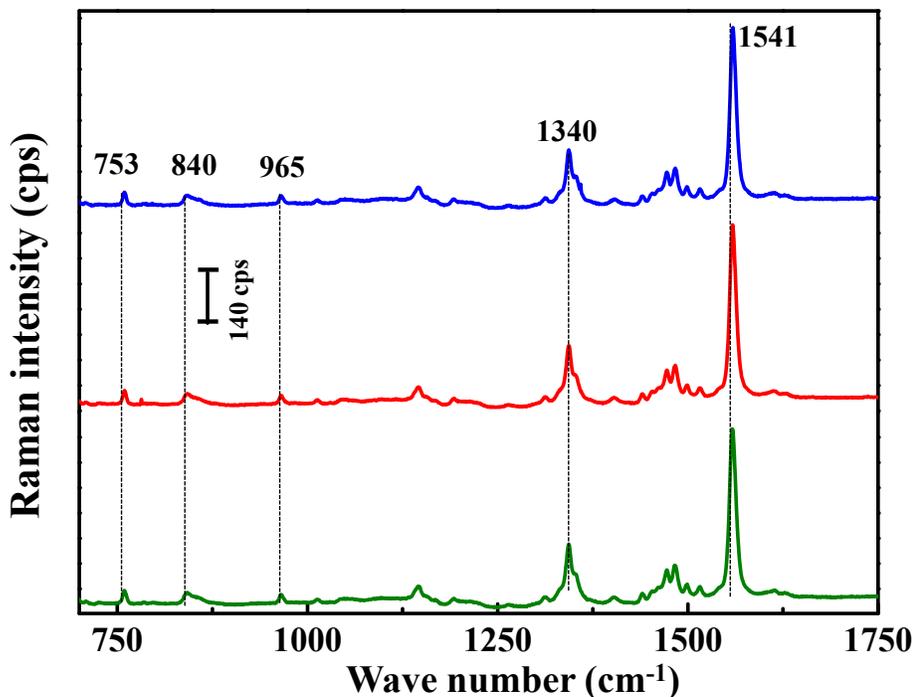


Figure S6: Raman Spectra of CoPc films of thickness 60 nm at different locations.

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